MKN

BLACK LIQUOR RECOVERY BOILER SYMPOSIUM 1982

Helsinki, Finland
August 31 – September 1, 1982

The Finnish Recovery Boiler Committee
The Finnish Energy Economy Association
EKONO Oy

TABLE OF CONTENTS

BLACK LIQUOR RECOVERY BOILER SYMPOSIUM 1982

Session A

Session B

Session C

Session D

---

1) To be distributed separately

CONVENTIONAL BLACK LIQUOR RECOVERY BOILERS TODAY

T. Roos, EKONO Oy, Helsinki, Finland

1. Introduction

The black liquor recovery boiler is the most expensive part of a single line pulp mill and spare capacity is normally not available. Accordingly any discontinuity in the recovery boiler operation incurs big production losses. The risk for explosions, of either the smelt-water or gas/oil type, is always present. Therefore it is no wonder that a great deal of effort has been expended to improve the recovery process and make recovery boiler operation as safe as possible. In many countries special committees dealing with recovery boilers have been formed and many symposiums have been held.

2. The Use of Black Liquor Recovery Boilers in Different Countries

Black liquor recovery boilers can be found all over the world. Although available statistics contain no explicit listing of recovery boilers by country, it is possible to estimate their number from data in the following references:

- FAO: Pulp and Paper Capacities, Survey 1981-86
- BLRBAC: Minutes of Meeting, April 7 & 8, 1981, (USA, Canada)
- Reference lists for recovery boilers (main manufacturers)

In compiling the following tables, it was necessary, in cases where date was insufficient, to make "best guess" approximations, and accordingly these tables should be considered as an indication of black liquor boiler distribution rather than a country by country census.

TABLE 1. PULP PRODUCTION 1982 (FAO, 1981-1986).
WOOD SULPHATE + OTHER FIBRE + DISSOLVING (MOST SODIUM BASED)
IN 1000 METRIC TONS

AFRICA	
Algeria	110
Angola	45
Cameroon	70
Eqypt	85
Gabon	120
Kenya	60
Morocco	95
Nigeria	90
South Africa	860
Sudan	-
Swaziland	180
Tanzania	10
Tunisia	35
Total	1760

NORTH AMERICA	
Canada	10800
Cuba	70
Mexico	950
United States	42700
Total	54,520

ASIA + OCEANIA	
Australia	550
Bangladesh	100
Burma	15
China	7500
India	2200
Indonesia	70
Iran	70
Iraq	85
Japan	10000
Jordan	10
Kampuchea, Dem.	10
Korea, Dem.Peop.Rep.	95
Korea, Republic of	120
New Zealand	750
Pakistan	90
Philippines	250
Sri Lanka	30
Syria	30
Thailand	65
Turkey	320
Viet-Nam, Soc. Rep.	40
Total	22,400

SOUTH AMERICA	
Argentina	470
Brazil	3600
Chile	650
Colombia	210
Ecuador	15
Paraguay	10
Peru	240
Uruguay	20
Venezuela	120
Total	5,335

EUROPE + USSR	
Albania	5
Austria	515
Belgium, Luxembourg	240
Bulgaria	320
Czechoslovakia	740
Denmark	140
Finland	5000
France	1500
German Dem. Rep.	850
Germany, Fed. Rep.	190
Greece	30
Hungary	90
Italy	750
Norway	620
Poland	650
Portugal	940
Romania	800
Spain	1400
Sweden	6500
United Kingdom	130
USSR	8000
Yugoslavia	550
Total	29,960

TABLE 2. ESTIMATED NUMBER OF BLACK LIQUOR RECOVERY BOILERS IN THE WORLD.

	Pulp Production (Most sodium based) 1000 tons	Number of Boilers
Africa	1760	15
North America	54520	430
South America	5335	45
Asia + Oceania	22400	110
Europe + USSR	29960	170
Total	113,975	770

TABLE 3. DISTRIBUTION OF BLACK LIQUOR RECOVERY BOILERS IN THE TOP ELEVEN COUNTRIES.

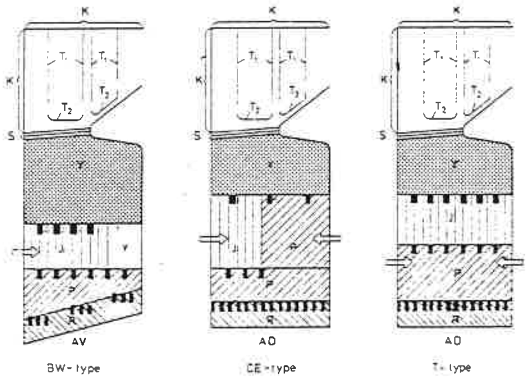
	Number of Boilers	% of Total (770)
USA	352	46
Canada	74	10
Japan	62	8,1
USSR	40	5,2
Sweden	35	4,5
Finland	30	3,9
Brazil	25	3,2
China	20	2,6
India	10	1,3
France	10	1,3
Spain	10	1,3
Total	668	86,8

3. Design and Construction of the Conventional Black Liquor Recovery Boiler

Almost half of the recovery boilers in use are located in USA. Canada, Scandinavia (including Finland) and Japan each contain about 10 % of the population. Geographical location has naturally had an influence on the construction and design of recovery boilers. The following figure and table describe the three main types of furnaces in Scandinavia.

FIGURE 1.

Zones in the Main Types of Recovery Boilers



AD = decanting bottom
AV = sloping bottom
R = reduction zone
P = burning zone
J = afterburning zone
Y = upper zone
K = superheater zone (furnace walls)
S = water cooled screen

TABLE 4. MAIN DIFFERENCES IN DESIGN OF BLACK LIQUOR RECOVERY BOILERS

	USA + Canada		Scandinavia (incl. Finland)		
	CE	BW	Ahlström CE	Götaverken BW	Tampella
Decanting bottom	+	−	+	−	+
Liquor nozzle					
- numbers	4-12	1-2	4-12	1-2	2-10
- oscillating	+	+	+−	+	+−
- plate	−	+	+	+	+
- wall spraying	−	+	−	+	−
Air distribution					
- primary	+	+	+	+	+
- secondary low	−	+(−)	+	+(+)	−
- " high	−	−(+)	−	−(+)	+
- tertiary	+	+	+	+	+
- nozzle control	−	−	+	+	+
Composite tubing	−(+)	−(+)	+−	+−	+−
Direct contact evaporator	+(−)	+(−)	−(+)	−	−(+)
Electr. precip.					
- dry bottom	−(+)	−(+)	+	+	+
Superheater					
- panel type	+	−	+	−+	−+

+ in use	(+) seldom in use
- not in use	(−) seldom not in use

Which type and design are the best? Each manufacturer claim that his design and construction are superior and provide an optimal solution for any application. From my experience I have developed some preferences but the recovery boiler process is very complex and not easy to understand and control. If I had to run a boiler I would

first like to have tools to control the process. By tools I mean the mechanical means to control the liquor spraying, air distribution in the furnace, heat surface cleaning, etc. I would then try to utilize these tools in such a way as to keep the boiler running at optimum conditions. Today we do not have all the tools we would like but using what tools are available make, in cases where the recovery boiler is a bottle-neck, the use of computer control in operating the recovery boilers economical.

For protection of recovery boilers I would refer to the recommendation of the Finnish Recovery Boiler Committee, published by EKONO and summarized in the following table.

TABLE 5.

Recommendation for Protection

The protection periods are stated with reference to normal kraft liquor and to a boiler drum pressure range of 50...100 bar (700...1 300 psi).

Protection Method	**Boiler Zone**							
	AD	AV	R	P	J	Y	K	S
Composite tubes	>20	>20	>20	>20	>20	−	−	−
Carbon steel tubes								
– Austenitic clad welding	−	−	~10	~10	>10	−	−	−
– Tight studding (without repairs)	~20	~6	3...6	3...6	3...6	−	−	−
– 17% Cr-steel flame spraying	−	−	<1	<1	1...3	3...6	−	−
– Metcoloy 405/5 flame spraying	−	−	<1	<1	1...3	3...6	−	−
– 2 mm (.08") corrosion allowance	10...20	3...6	1...3	3...6	3...6	~10	~20	>10
– 4 mm (.16") corrosion allowance	~20	6...10	2...5	6...10	6...10	~20	>20	~20

Recommended protection method is indicated with a circle.

The numbers mean protection period expressed in years which has been practically verified or estimated. – = protection unnecessary.

AD = decanting bottom
AV = sloping bottom
R = reduction zone
P = burning zone
J = afterburning zone
Y = upper zone
K = superheater zone (furnace walls)
S = water cooled screen

(see Figure 1.)

I am convinced that international exchange of information and cooperation in research and development will lead to the development of a reasonable, reliable, safe and efficient recovery boiler. In the future the conventional boiler may be replaced by some new type of equipment or process but we can expect to have the conventional black liquor recovery boiler with us for many years to come.

ACTIVITIES IN THE RECOVERY BOILER FIELD

- RECOVERY BOILER ACTIVITIES IN U.S.A.
  by T.M. Grace, Institute of Paper Chemistry, Appleton, U.S.A.
- REPORT ON THE ACTIVITIES OF BLRBAC TO BLACK LIQUOR RECOVERY BOILER SYMPOSIUM 1982
  by I.V. Paldy, Domtar Inc., Montréal, Canada
- REPORT FROM THE SWEDISH RECOVERY BOILER COMMITTEE
  by J.-E. Olsson, MoDoCell AB, Örnsköldsvik, Sweden
- REPORT OF THE FINNISH RECOVERY BOILER COMMITTEE
  by P. Valkamo, Enso-Gutzeit Oy, Imatra, Finland

Papers to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

A2

REPORT FROM THE SWEDISH RECOVERY BOILER COMMITTEE

Jan-Erik Olsson, Managing Director
MoDoCell AB, Örnsköldsvik, Sweden

1. Abstract

The Swedish Recovery Boiler Committée was established in 1965. The reason being the wish from many people in the pulp industry to improve the exchange of information about recovery boilers and problems connected to them.

The members of the Committée have a very broad back-ground, which gives a guarentee for a successful work.

2. Introduction

The committée is comprised of engineers from the industry, people from ÅF, Götaverken, The Swedish Board of Occupational Health, representatives from the Labour Unions and from authorities responsible for the control of recovery boilers. So the members together have a very broad practical and theoretical knowledge which gives a guarentee for a successful work.

The committée was established in 1965. At the beginning the main task for the committée was to find out the best way to close down a recovery boiler in the event of an emergency situation arising. During the past years we have also covered other areas as training programs for operators, R & D-questions and information.

2.1 Activities

Some of the most important tasks for the Swedish Recovery Boiler Committée are as follows:

2.1.1 Improve security in recovery boiler operation

2.1.2 Push the development towards improved efficiency and availability of the recovery boilers

2.1.3 Push questions concerning training of personnel

2.1.1 Ever since the beginning security questions have had a central role in the work done by the committée. The results of the work are published as "Recommendations" or "Information". These are distributed to people at all the pulp mills in Sweden and to other contact persons, also here in Finland.

Collection and distribution of information concerning near-accidents and accidents is also very important to prevent, if possible, the same mistakes being made.

Discussions and evaluations of these reports have most certainly improved the security in recovery boiler operation.

2.1.2 Within the committée many initiatives have been taken which have lead to improvements in the design and construction of recovery boilers and the systems around them.

Practical experiences and theoretical knowledge within the committée have been of utmost importance in this work.

Different R & D-projects have been supervised by the committée. One of the best known is the KASEX-75 project concerning smelt-water-explosions. This project demonstrated the enormous force unleashed when water and smelt are mixed in an uncontrolled way. The results from this project will now be used in a new project concerning ideas about how to design boilers and houses to avoid serious damages in case of a smelt-water-explosion.

2.1.3 During the years, the size of the recovery boilers has increased dramatically. Very often a pulp mill has only one big unit, which means that the availability and efficiency must be kept at a high level. If not, the production economy in the mill will deteriorate very fast. Thus, it has become increasingly important to have highly trained operators to meet the above mentioned demands.

Pollution abatement and higher energy costs also means that the operators must be highly qualified for these jobs.

The committée has started a study of the use of simulators in training of personnel in handling different situations when running a recovery boiler. Using present computer technology it ought to be economically feasible to develop a simulator for training of operators.

2.2 International contact

We have, for many years , had a very close contact with EKONO (Finland), which has a representative in our committée. Exchange of information and experiences between the two countries about recovery boiler operation has been of great importance during the past years.

We have also a close contact with two committées in the United States, both involved in questions concerning recovery boilers, a contact which was established a few years ago. The two committées are API (American Paper Institute) and BLRBAC (Black Liquor Recovery Boiler Advisory Committée).

Exchange of information goes on through reports and papers given at the API and BLRBAC annual meetings in USA.

3. Summary

Last year we made an inquiry among the pulp mills in Sweden to find out their views on the work done by the committée. The result of this inquiry was very encouraging. There seems to be a permanent need of information and exchange of experience about recovery boilers and questions related to them in our pulp industry.

Therefore we believe that even in the future the Recovery Boiler Committée will continue to play an important role in our pulp industry.

A2

REPORT ON THE ACTIVITIES OF BLRBAC TO BLACK LIQUOR RECOVERY BOILER SYMPOSIUM 1982

I.V. Paldy
Domtar Inc., Montréal, Canada

There are many distinguished groups who are dedicated to improve the design and operational efficiency of boilers used in the kraft pulping process.

The primary concern of the Black Liquor Recovery Boiler Advisory Committee is safety. The goal is the elimination of explosions that are not only costly but unallowable hazard to operating personnel.

Unfortunately, present problems of operation and safety of recovery boilers are far exceeding those of conventional power boilers. The mechanisms of the smelt-water reactions are still not thoroughly understood, but the safety principles required to eliminate the introduction of water or weak black liquor into a furnace containing molten smelt, have now been identified.

BLRBAC was formed in 1962 by North American representatives of the Pulp & Paper Industry, two boiler manufacturers and Insurance Companies providing coverage on black liquor recovery boilers. Since the first meeting the membership has been enriched by the additional representatives from not only Canada and U.S.A., but also from the following countries: Argentina, Australia, Chile, Columbia, Finland, Japan, Kenya, Phillipines, South Africa, Spain and Sweden. More recently, representatives of several Consulting Engineering Firms have been accepted as Continuing Guest.

BLRBAC meetings are held twice a year usually in April and October with complete and free exchange of information. The average attendance at these meetings has grown to 200.

At each meeting all incidents reported from the previous six (6) months are reviewed, discussed in details and classified by the Emergency Shutdown Subcommittee. The number of North American incidents that have been classified to date as either a "CRITICAL EXPOSURE" or "EXPLOSION" are 188 and 120 respectively.

There are four additional subcommittees and two task forces engaged actively on six major subjects. These subjects are:

- Safe period for cooling smelt bed after an E.S.P.
- Continuing survey of rapid drains
- Instrumentation and controls
- Safe firing of Auxiliary Fuel
- Safe firing of Black Liquor
- Waste Stream in Recovery Boilers

The open panel discussion of the "operating problem session" gives participants the freedom to speak on any related subject, and provides an excellent opportunity for all to profit from the experience of others.

Other highlights of the semi-annual meeting are the special representation from the American Paper Institute, The Western Canadian Group of B.C., BLRBAC, Japan and Scandinavia. The importance of their reports and contribution to BLRBAC's work is well recognized.

Accomplishment To Date

In the past 20 years, much progress has been made. The safety measures that have been identified and developed by the various subcommittees have been compiled and published by BLRBAC.

These are as follows:

- Questionnaire on Recovery Boiler incidents
- Recommended Emergency Shutdown Procedure
- Questionnaire on Rapid Drains of Recovery Boilers
- Recommended Good Practice for "Safe Firing of Auxiliary Fuel".
- Guide to the Preparation of an Operator Training Manual and Preventative Maintenance Program.
- Recommended Rules for Personnel Safety, including the design and construction of Buildings & Equipment.
- Installation Check List and Classification Guide for Instruments and Control Systems.
- Recommended Good Practice for Fire Protection in Direct Contact Evaporators and Associated Equipment.
- Recommended Procedure for Testing Emergency Shutdown Systems.
- Recommended Good Practice for "Safe Firing of Black Liquor".

As a direct result of the work of the subcommittees and the adoption of specific recommendations, auxiliary - fuel explosions have been almost completely eliminated.

Notable progress has been also made in the design of boiler pressure parts, the acceptance of 100% X-Ray testing of Construction Welds, the reliability of liquor concentration measuring devices, the installation of rapid drain systems for not only the new, but older recovery boilers, d the design and construction of safer buildings in general, just to mention a few.

Due in part to BLRBAC's policy of free exchange of information & the extensive publication of its findings, corporate management has not only recognized the importance of the recommended safety measures, but now is more willing to allocate the necessary expenditures for safer recovery boiler installations. There are numerous plants where old and overloaded units are being replaced with new ones. The lower furnace water walls, constructed of corrosive resistant composition tubes, good feedwater treatment equipment, and many other improvements are being provided that were more an exception than a rule, only a few years ago.

Current Problems

While much has been accomplished, incidents and explosions are still occurring.

The most notable causes are:

- Introduction of weak liquor originated by equipment that has malfunctioned, human errors, etc.
- Introduction of water originated by local overheating caused by inadequately treated feedwater or improper acid washing, tube and attachment weld failures, smelt spout leaks, break of sootblower lances , human errors, etc.
- Overheating of boiler parts due to lack of feedwater or Fires in-turn caused by malfunctioning controls and/or human errors, etc.

What Remains To Be Done

BLRBAC will and must continue to review recovery boiler incidents, study their causes, coordinate development work and further encourage information exchange in the Industry.

The manufacturer of boilers must constantly review their design, shop quality control, procedures and field construction methods, to minimize the possibility of pressure part failures.

The owners must insist on adaptation of the BLRBAC safety recommendations and provide the funds for the necessary equipment. This to include also the enforcement of good coordination amongst the Engineers of the Owner, Consulting Firms, Suppliers, Inspection Authorities and Plant Operating Personnel.

The Mill Management must recognize that in addition to providing operating personnel with a safe place to work, they must also properly train their staff. If the sophisticated equipment they are responsible for is operated improperly, the results can be catastrophic. The operators should also feel totally confident that their judgement, especially in an emergency situation will not be second-guessed or questioned by their superiors.

Furthermore, management must also enforce the adaptation of properly planned preventative maintenance and comprehensive inspection programs that are supplemented with independent safety audits.

In conclusion, there are no plausible excuses for a Black Liquor Recovery Boiler Installation to lack the required hardware, to have improper procedures or to have an inadequately trained group of operators.

The sincere efforts of BLRBAC, the Equipment Manufacturers, the Owners, the Mill Management, the Operators and the Insurer will result in safer Recovery Boiler Installations by ultimately eliminating explosions.

The author wishes to credit Messrs. A.E. Logan and C.W. Connanay for portions of this report.

A2

REPORT OF THE FINNISH RECOVERY BOILER COMMITTEE

Pertti Valkamo
Enso-Gutzeit Oy, Imatra, Finland

1. Abstract

The corrosion study in 1965-1968 and some preliminary meetings of the recovery engineers were followed by a budgeted activity of the Finnish Recovery Boiler Committee since the beginning of 1969.

This paper will discuss the above corrosion study, the operation of the Corrosion Sub-committee, the R.B. Controlling Project, the performed and current projects as well as continuous activity of the Secreteriat.

2. Corrosion Study 1965...1968

The co-operation between the owners of the recovery boilers in Finland was started in the year 1965. The reason to it was the serious wastage of the furnace wall tubes which was first time realized in the year 1961 soon after some boilers with 68...85 bar steam pressure having no furnace tube protection had been taken in operation.

The beginning of the co-operation was corrosion study which was completed during 1965...1968. The final report of the above study /1/ contains still today useful information.

The tests in the existing furnaces were one of the most important areas of the above study. The numerous testing sections installed either in the shop or in the field gave important information. Some tested protection methods gave poor results but some could be included in the recommendation published in the final report.

E.g. the austenitic clad welding and different types of flame spraying belonged to the first recommendation and are used still today although composite tubing has been the most important method in Scandinavia and Finland since 1972. B&W boilers had been furnished with studded lower furnace tubes already before the Finnish study and studding was included to our recommendation also.

The first composite tubes were installed in a C-E boiler in the Kaukopää Mills at the beginning of 1968. No results could, however, be published in the 1968 report because of the short testing period.

The study in question discussed also the corrosion outside the furnace tubes. Gastight sealing was found to be a reliable protection method.

3. Budgeted Co-operation

The corrosion study had given good results of the co-operation between the mills. The annual meetings of the energy engineers did not leave enough time for the special questions in the recovery area. Some meetings were arranged during 1966...1968 for discussing recovery boilers more profoundly.

The above development led some persons to a proposal for a continuous co-operation which should have its own budget. This type of co-operation was started in the beginning of 1969 and so the Finnish Recovery Boiler Committee, FRBC, had born.

The following organizations have been in the co-operation from the beginning:

All the mills having recovery boilers
Ahlström and Tampella
EKONO Oy
The Finnish Pulp & Paper Research Institute

The Finnish insurance companies have supported the Finnish Recovery Boiler Committee also.

Finnish Recovery Boiler Committee had in the beginning four sub-committees. However, it was realized later that it was better to have

only the Corrosion Sub-committee and take care of the other duties with using the secreteriat at EKONO or with temporary working groupes founded and dissolved according to the projects.

3.1 Corrosion Sub-committee

The corrosion sub-committee is working with the corrosion questions and publishing annually the recommendation for the tube protection. The recommendation was revised quite often before 1978 but later we have had only minor changes after composite tubing seemed to give secure protection in the lower furnace.

Carbon steel tubes with heavy wall thickness have been recommended for the upper furnace and screen.

The recommendation was published in English 1978 and is valid still today. However, we feel we have not enough experiences about the studded tubes in Finland. There are different opinions about the following subjects:

Stud material
Stud diameter
Repairing method

We have recommended alloyed 10 mm studs repaired with a welding pistol but some poor experiences exist.

The alloyed studs very often do not give better results than the carbon steel studs. The 12,7 mm studs can give better protection than the 10 mm studs /2/. Finally welding of a new stud on the worn one has often caused loosening of the old stud from the tube.

3.2 Controlling Sub-committee

A very important and valuable project of the Finnish R.B. Committee was the controlling project 1971...1973. Although it took more than one year after the final report before the first project was started in Kaukopää the above study has later led to a great amount of the recovery boilers under computer control in Finland.

3.3 Current Work of FRBC

The existing budget of the Finnish Recovery Boiler Committee is 110 000 USD. It is used besides for the work of the Secreteriat for the different projects.

3.31 Projects

During the latest years the following projects have been completed:

Unsymmetry in the R.B. Furnace
Comparison of Smelt Dispersion Methods
Study about R.B. Emissions
Experiences about Sonic Soot Blowing
Control of the Safety on the R.B. Gasside

The projects were selected according to an inquiry to the members. The following projects are still to be continued:

Water Soot Blowing
Black Liquor Study

Black Liquor Study was the subject having the strongest interest in the above inquiry. The costs of it, 180 000 USD, demanded dividing the project for several years. The first subject will be discussed in this symposium, the remaining studies belong to the program of the future years.

Wood Raw Material and Cooking Conditions
Uncommon Make-up Chemicals and Side-flows
Final Evaporating
Mill Studies
(On-line Viscosimeter)

3.32 Training

The laws and standards concerning the boiler operators are very general in Finland. Some demands are given to the superintendent of the steam and plant and subsequently he will be responsible qualified persons are selected to operate the boilers.

There are no instructions about special courses or examinations for the boiler operators. The existing examinations are meant for the chief engineers responsible for the small plants.

FRBC has tryed to improve the situation with publishing a set of books for the chemical recovery. The mills are able to organize their courses using the above material which includes an exercise book also.

The co-operation with the Swedish video-group was studied twice but without a positive result because of the high costs and the existing poor economical situation.

The amount of the R.B. explosions is very low in Finland. We have had three smelt-water and four gas explosions.

The reason has probably been rather good luck than the training system. One more reason good be that the Finnish boiler operator holds his position quite long time without changing his duties.

3.33 International Co-operation

The international co-operation has a great value in the work of FRBC. We have the widest experiences about the co-operation with the Swedish R.B. Committee. We have a continuous contact with BLRBAC and API R.B. Committee also.

3.34 Information System

The information to the members is distributed by the Secreteriat. We receive about 12 times annually the news about the articles published in the recovery area and later the complete list abstracts and keywords of all the information published during the year.
Finally a system shall be created for finding the reports published during the Finnish R.B. co-operation.

3.35 Reporting System

The mills are reporting about the major failures of the recovery boilers and these reports are then distributed to the members.
Fortunately there are only a few such reports published every year.

We have also studied a system for reporting the smaller damages, coding them and reporting using automatical data processing. However, the system looked too complicated and seemed to demand too much work in the mills.

It has been discussed whether the above smaller problems could be treated in the annual meetings of the chief engineers and these discussions then reported by the Secreteriat.

4. Experiences about R.B. Committee

The co-operation in the Finnish Recovery Boiler Committee is presuming all the mills having recovery boilers participate in this work. So far all members have seen the performed work so useful that regular co-operation has been continued nearly 14 years.

If I had to select today the most important subjects of the previous and current committee work I would suggest:

- corrosion studies
- controlling studies
- information system
- black liquor research
- unofficial information.

References

1. Finnish Recovery Furnace Corrosion Research Committee: "Study of Corrosion Phenomena in Recovery Boiler, 1965...68", Main Report October 23, 1968.

2. J.A. Dickinson, M.E. Murphy, W.C. Wolfe: "Kraft Recovery Boiler Furnace Corrosion Protection", TAPPI Engineering Conference, Atlanta, GA, Sep. 28 - Oct. 1, 1981.

TAILOR-MADE RECOVERY BOILERS

by

C. MacCallum, P.Eng., Senior Supervisor
Sandwell and Company Limited, Vancouver, B.C., Canada

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

TAILOR-MADE RECOVERY BOILERS

COLIN MacCALLUM, P.ENG.
Senior Supervisor

SANDWELL AND COMPANY LIMITED
Vancouver, B.C., Canada

ABSTRACT

The technology exists today for designing a recovery boiler which will require minimum maintenance and which will give trouble-free operation between shut-downs. The early selection of a number of key design elements has a major impact on its lifetime operating efficiency.

This paper highlights some of the more important design features such as the size of the furnace cavity, the radiant boiler principle, and desirable construction details of furnace exit screens, superheaters, generating banks and economizers. A sophisticated load duration curve analysis method is recommended for the optimization of flue gas exit temperatures, and for the selection of steam-or-water air heaters. Some guidelines for the selection of non-pressure parts are given. Flue gas tempering is proposed as a means of controlling fouling in heating surfaces under conditions of unbalanced gas temperature and/or high load operation.

KEYWORDS

BOILERS: RECOVERY: RECOVERY FURNACES: DESIGN: RADIANT: SUPERHEATERS: GENERATING BANKS: ECONOMIZERS: AIR HEATERS: FANS: GAS TEMPERING: FOULING: LOAD DURATION CURVES: OPTIMIZATION.

INTRODUCTION

Design errors become incorporated in recovery installations through a lack of awareness or attention to detail on the part of all participating parties. The solution is the custom design of the unit to suit the requirements of each client, through the careful selection of the most desirable design features at the earliest stages of a recovery boiler project - before the boiler is purchased.

Traditionally, consultants prepare bid comparison summary sheets on which the equipment and performance details of the recovery boilers offered by various manufacturers are presented for client review prior to final selection. These data are essential for a satisfactory comparison, but a great deal of valuable information can be obtained from an examination of the proposal drawings and the explanatory detail drawings which may be requested from the manufacturer. The following review, in sequence from furnace to stack, highlights features of recovery boilers on the market today, with particular emphasis on those from North American suppliers.

JRNACE

nple total furnace heating surface is essential for successful operation, but, contrary to
pular belief, the ratio of furnace height to furnace cross-sectional area does not, within
nits, appear to be critical to good operation, at near nominal design load. It has been
tablished that boilers having a small hearth area in combination with a high furnace,
spension firing, and tangential secondary air admission, have similar overload capability
boilers having a large hearth area and lesser height, used in combination with the
mlinson method of spraying on to the walls of the lower furnace, with minimal
spension burning, and with non-tangential air admission. One consideration other than
erload capability which is directly associated with these two distinct firing methods and
rnace configurations includes the somewhat greater sensitivity of the smelt reduction
te to boiler load, combustion air temperature, and mode of operation in units with
ngential air admission. The relatively high degree of gas temperature unbalance across
e furnace width is often cited as being a major disadvantage of the tangential air
mission design, but because the phenomenon is inherent in the design, allowance can be
ade for superheater unbalance, and for minor gas temperature unbalance in succeeding
rts of the unit. Excessive gas-temperature unbalance at high boiler loads may however
harder to overcome.

e furnace heating surface should be selected with regard to the operating load range
ich may be expected. In an excessively large furnace, the degree of smelt reduction
ay be unacceptably low, particularly if the calorific value of the liquor is lower than
ticipated. If a great deal of operation at low loads is anticipated, for example during the
st years of operation, then guarantees should be obtained for the degree of smelt
duction at the low loads, together with a guarantee that the unit will operate at the low
ads with no supplementary fossil fuel.

ere are factors other than the relationship between hearth area and furnace height,
ich affect the design more profoundly. Since the recovery boiler market place is highly
mpetitive, the design margins and the overload capabilities of the boilers have gradually
en reduced as more and more operational data have been analyzed. The boiler is
signed, and the guarantees are made, for a particular black liquor solids analysis, which
ay prove to be very different from the analysis experienced in practice. The guarantees
ust contain a clause which permits the normal arithmetical corrections for liquor
viations to be made when the boiler is tested and the fulfilment of the guarantees is
der review.

ajor deviations from black liquor solids design heating values can cause considerable
rformance shortcomings:

If the heating value in practice proves to be substantially lower than the design value, the following problems can be expected:

- Increased risk for furnace blackouts, especially at low loads, and at low solids concentrations
- Low furnace hearth temperatures which result in low reduction rates and high SO_2 and TRS (total reduced sulfur composites) emissions
- Slow combustion of solids in suspension
- High risk for fouling in the superheater because of the high total solids quantity caused by the high ratio of inorganics.

b. If the heating value is substantially higher than the specified design value:

- High furnace hearth temperatures result in high sodium fume emission from the bed and high carry-over and superheater fouling can again result
- Corrosion of furnace wall tubes and studs is accelerated because of the increased temperature in the hearth zone.

A series of careful liquor tests should be conducted prior to the preparation of the specification for the unit. If such tests create any suspicion that a large range of heating values may be expected, it is strongly advisable to request that the design should cater for the full range of heating values. Additional furnace height above the manufacturer's "standard" should be purchased. The adage "If in doubt - add 10 feet" is worth remembering - even in S.I. units.

The lowest possible furnace exit gas temperature, that is, the largest furnace possible, commensurate with reasonable additional capital costs, is a first-class investment, in that for any one design of boiler, superheater fouling will be held to a minimum and the overload capability of the boiler will be maximized.

While we are on the subject of the furnace, there is no doubt that the fully-welded gas-tight furnace wall is the only acceptable construction presently available, and that composite tubes are preferable to mild steel tubes for higher pressure boilers. The stainless steel sheath on a mild steel tube, or so-called co-extruded or composite tube, has a proven record of no corrosion and minimum downtime in many units since the first installation at ASSI, Lövholmen, in 1971. There is no question either that furnace-side corrosion becomes a major concern in high-pressure units: For example, there are many units operating at 6,3 MPa which have suffered the ignominy of having the entire lower furnace replaced after a mere 10 or 12 years of operation. Several of these units have featured replacements with composite tubes. Composite tubes therefore, appear to be highly advisable in units operating at this pressure and above.

Because of the cleanliness of the gas side of the lower furnace tubes on a unit with composite tubes, downtime for inspection may be reduced without prejudicing safety. Such operating cost savings alone may justify the use of composite tubes even at lower pressures.

Other features of furnace design which should be considered include the following: Rounded furnace corners have a decided advantage over square corners where the corner tube is in the radiation shadow over its full height and may suffer from poor circulation: A well-defined nose arch can greatly improve gas flow in the superheater: A retractable safety-roof can appreciably shorten the time required for inspection of the upper furnace and superheater: In units with sloping furnace-floor tubes, a common header serving the sloping floor tubes and furnace rear wall eliminates the risk of smelt breakthrough at the junction of the floor tubes and front wall tubes: In units with decanting furnaces, modern units employ a continuous floor tube to eliminate smelt breakthrough at the centre of the floor: The furnace front corners above the level of the furnace nose should be specially designed to rupture along the junctions of the adjacent corner tubes without rupturing the tubes, to minimize damage to the unit in the event of an explosion in the furnace.

·URNACE EXIT SCREEN TUBES

ı modern recovery boilers, superheater cavities as high as 15 m are common and a smelt ump falling from the roof is travelling at some 60 km/h on impact with the screen tubes.

ı the extreme case, an individual tube will shear and a water/steam mixture will be jected from both broken ends under full boiler pressure into the furnace. This may result ı a smelt-water explosion with further damage and possible loss of life. For a 1000 t/d nit, an outage can mean a net loss of more than $200 000 per day and an extended hutdown normally results from a smelt-water explosion. Extra-thick walls in the ppermost screen tubes, and the incorporation of the tubes into a beam-like construction re measures commonly used to combat tube shear and tube deformation.

nlike furnace tubes, the screen tubes are heated over the greater part of their ircumference and, in the sloping portion receive heat mainly on the underside in the form f radiation from the furnace cavity . High water velocities are essential to prevent eparation of steam bubbles from the water-steam mixture within the tubes which causes team blanketing, poor cooling of the tube wall, and eventual failure. Screen tubes are also able to tube overheating and failure as a result of solids deposition during circulation isturbances or disruptions in the feed-water treatment plant.

he steam-cooled furnace exit screen concept, in effect the elimination of the screen per e, in chemical recovery boilers in the pulp and paper industry was developed to combat hese hazards inherent in the conventional water-cooled design, and has been presented arlier by MacCallum (1).

ore than 20 units are now in successful operation with screen tubes in the conventional cation but cooled with steam, or with no screen tubes at all.

JPERHEATER

ıe widely-spaced platen (tangent-tube) design superheater is close to ideal for recovery ilers. Each multi-tube superheater element across the width of the boiler consists of bes which are virtually tangent to one another in the direction of gas flow to minimize ubborn bridging of salt-cake between adjacent tubes. From a theoretical heat transfer int of view, the design is less effective than a spaced tube surface, but the much lower uling tendencies of the platen superheater make it more attractive operationally, rticularly if chlorides are present in the black liquor.

wide side-to-side spacing of the superheater elements minimizes superheater fouling, but compromise between maximum cross-spacing and reasonable capital costs has to be ruck by the boiler designer. In high pressure units the high temperature conditions at the perheater steam outlet are equivalent to a large temperature drop in the flue gases, as ey pass through the superheater section; the designer can then readily eliminate the ater-cooled screen even if his particular design standards normally include a screen. The ssibility may also exist of reducing the cross-spacing of the superheater banks in the wer gas temperature regions. This principle is used throughout the recovery boiler.

The widely-spaced superheater has the additional advantage of providing a more radiant operating characteristic than the more closely spaced superheater - that is, the natural variations in the outlet steam temperature are smaller, and the steam temperature control range can be larger for a given capacity of attemperator.

ATTEMPERATOR

An attemperator for superheated steam temperature control is often considered to be a luxury when the steam temperature is below about 400°C: The outlet steam temperature varies considerably however, from a clean superheater condition at start-up to a relatively dirty superheater condition at the end of a long production run. If no inter-stage attemperator is provided, then excessively high steam temperatures can occur at the beginning of the run and damage the superheater, or the low temperatures at the end of a long production run can mean a loss of in-house power generation.

As a general rule, an attemperator should be provided when a turbine generator is installed in the mill, and the recovery boiler is expected to provide a large proportion of the turbine steam. With steam temperatures above 400°C an inter-stage attemperator is normally used, but with lower steam temperatures an attemperator at the outlet of the superheater is often employed, although an attemperator at the superheater outlet does not protect the superheater in any way. An inter-stage attemperator is always to be preferred.

For an inter-stage arrangement, either a Dolezal attemperator which uses condensed steam from the steam drum as the spraying medium, or a fully-welded attemperator of indirect type is much to be preferred to one which uses direct-spray of feed-water because unexpected upsets in the demineralizer plant can cause raw water to be sprayed into the superheater and tube burn-out can result.

BOILER GENERATING BANK

The transition zone between the widely-spaced superheater elements and the closely spaced tubes of the generating bank requires particularly close design attention if fouling under overload conditions is to be avoided.

600°C has long been considered in many recovery boiler design offices, as the maximum allowable gas temperature entering the closely spaced tubes of the generating bank: This limit, above which the particulate in the flue gas is soft and tends to adhere to heating surfaces, has dictated the design of the upstream surfaces of furnace and superheater. In fact, this temperature limit applies to any closely-spaced heating surfaces.

Where a small superheater is installed, and/or in cases where there is no water-cooled screen at the furnace exit, the gas temperature entering the generating bank may be higher than the 600°C mentioned above. In this case, the cross-spacing of the front rows of the boiler bank can readily be increased to compensate for the smaller total surface upstream. The loss of generating bank heating surface is then compensated for by additional economizer surface to maintain the desired flue gas exit temperature.

ıe neatest and most foul-proof design takes the tubes of the furnace rear wall and perheater cavity floor directly into the water drum. Many of the present designs where e tubes of the furnace rear wall and superheater cavity floor are bent to form a screen tween the superheater and the generating bank, would be much improved, were the tubes this screen lined up both with the tubes of the superheater and those of the first rows of e generating bank. For example, with some present arrangements the superheater ements are on 305 mm spacing, the screen is on 204 mm spacing, and the generating bank on 127 mm spacing, which creates a clear conflict with the sound principle of keeping bes in-line, and which is particularly bad where there is no intervening cavity between rtions of separate heating surfaces.

a hopper is employed below the generating bank, another detail which deserves attention that at least 300 mm clearance must be provided between the lower ends of the tubes of e boiler generating bank and the upper ends or slopes of the hopper: When the hopper ate is hard up against, or close to, these tubes, a potential site for fouling is created.

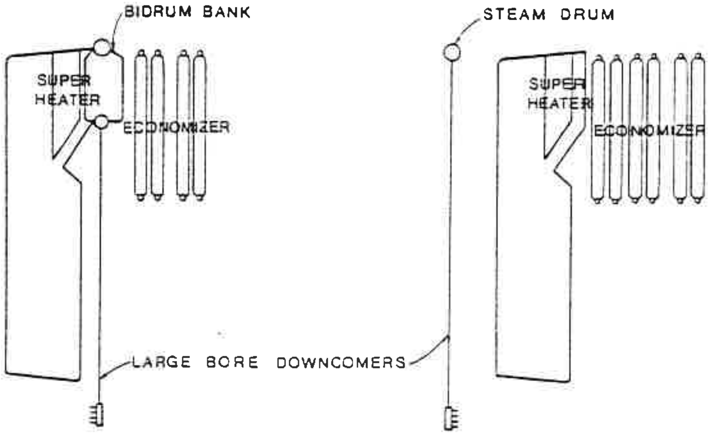
ıe single-pass boiler bank, which offers no obstructions or changes in direction to the flue ıses, is always preferred over two-pass or multi-pass designs. As always, changes in rection, and flue gas baffles are to be avoided in areas of relatively high gas velocity.

t this point it is worth noting that double-sized access doors speed inspection and aintenance, and should be a feature of every boiler - whatever the width.

ADIANT CONCEPT

onventional kraft recovery boilers feature a bi-drum design, with a steam drum and a ater drum interconnected by a large bank of closely spaced generating tubes. These nerating tubes are expanded into tube holes in the two drums primarily because a fully-elded construction would require individual welded stub nozzles for each tube on the thick um shells, and this would be prohibitively expensive. In the radiant design the generating nk is entirely eliminated and replaced by an additional two banks of fully-welded onomizer tubes, see Figure 1.

Figure 1 - Bi-drum and Radiant Boiler Salient Features.



The radiant design, which has been proven on boilers having similar fuel bed characteristics, when compared with the bi-drum design is equally responsive to load changes, and has the following advantages:

1. Overall project time could be reduced by 1 - 2 months ($3 000 000 gross profit per month for 1000 tons/day and decreased interest charges which could themselves amount to $800 000 per month on a $50 000 000 project)
2. Lower total manpower peak and total erection manhours
3. Lower capital cost at higher operating pressures - perhaps 5 percent at 6,3 MPa
4. Capable of shorter start-ups and shut-downs
5. Fully-welded construction
6. Insensitive to ESP rapid drain and low water level excursions
7. Smaller rapid drain valves can be employed for the furnace since there is no generating bank.
8. More economical use of sootblowing steam
9. Shorter downtime in the event of a catastrophic steam drum failure.

For direct-contact recovery boilers at all pressures, and for low-odour boilers at higher operating pressures, the demand for safer recovery boilers and shorter project times favours the radiant design. The design is presented in more detail by MacCallum (2).

A variation on the same theme is the fully-welded, modular generating bank, which will make its debut in the Götaverken boiler at Great Northern Nekoosa when it starts up in 1983.

FLUE GAS TEMPERING

As mentioned earlier, excessive gas-temperature unbalance across the width of the unit may prove troublesome. The temperature differential can persist through the entire unit, to a decreasing degree towards the ID fan. The phenomenon can lead to plugging of the closely-spaced heating surfaces of the boiler bank and economizer, can cause undue fouling of direct-contact evaporators, and can lead to appreciable differences in the effiendency of the twin electrostic precipitators. The problem is aggravated at high boiler loads, and towards the end of production runs if the unit displays a tendency to persistent fouling and increasing gas temperatures.

One solution which could be considered is the introduction of a flue gas tempering system. The system would recycle cool flue gas from the outlet of the precipitator to ports across the width of the front wall of the upper furnace, opposite the superheater inlet. This system is a feature of some utility boilers for reheat temperature control, but in the chemical recovery boiler it would be used to control flue gas temperatures and fouling as indicated above. The principle is shown in Figure 2.

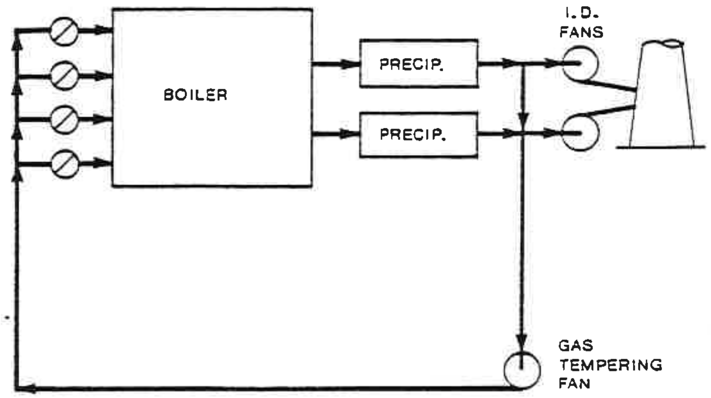


Figure 2 - Flue Gas Tempering for Control of Gas Temperature and Fouling

)PPERS

common requirement for the design of hoppers is that the hopper slope should be a .nimum of 55° from the horizontal. To obtain an effective valley angle of 55° in a ramidal black-liquor-sluiced hopper the nominal slope must increase to about 65° which sults in a much deeper hopper. Pyramidal hoppers are not recommended for dry ash moval.

y ash removal using full-width hoppers is very common on low-odour boilers. All hoppers quire inspection doors and access doors, but pyramidal black-liquor-sluiced hoppers also quire rodding ports.

concrete floor should be provided at the level of the bottom of the hoppers to prevent uor or salt-cake from cascading down through the boiler house in the event of hopper ılfunction.

e clearance between the lower ends of tube banks and hopper slopes must be at least 0 mm, as noted earlier.

:ONOMIZERS

oss-flow economizers with poorly-located baffles are a source of continual fouling blems, and poor design in this area often is a major obstacle to high load operation. ese problems may be solved, after the fact, to some degree by the installation of ditional sootblowers and the expenditure of large quantities of sootblowing steam. A newhat better design of cross-flow economizer has only two baffles. In the cross-flow sign, the plate wall at the rear of the economizer should not be hard up against the rear e of the bank, because of increased risk for fouling initiated between the rear row of es and the rear wall of the enclosure. An access cavity should be provided at the rear the bank.

Also where the rear wall plate of the economizer enclosure and the lower cross baffle meet, a full-width damper forming the rearmost portion of the baffle between the economizer tubes and the rear wall plate should be provided: This damper should be timer-operated, say once every five minutes to get rid of any material which would otherwise have accumulated on the rearmost portion of the baffle.

The most satisfactory design of the economizer from a fouling and sootblowing steam conservation standpoint is the longitudinal-flow non-baffled economizer. The tube surface is less effective in longitudinal flow than in cross-flow and a certain premium for the additional heating surface and draft loss has to be paid. This premium must be weighed against the advantages of reduced fouling and reduced consumption of sootblowing steam.

Whether the economizer is in cross-flow or in longitudinal flow, the banks must be correctly orientated, to avoid unnecessary fouling. If the banks are asymmetrical, for example in designs where access cavities are provided within the upper and lower ends of each bank, the correct orientation of the economizer banks is important.

It is self-evident that the economizer modules must be able to expand freely within the casing structure, and that the tube-to-header welds must be of high quality.

OPTIMIZATION OF FLUE GAS EXIT TEMPERATURES

It is clear that additional steam which can be generated in the recovery boiler is steam which need not be generated in the power boiler, generally from oil or natural gas: In other words, heat recovery in the recovery boiler should be optimized. Unfortunately, the flue gas exit temperature is often selected arbitrarily by either the client, the consultant or the manufacturer with only cursory regard for the feedwater temperature, and an approach temperature of say 30 to 40°C. However, the optimum gas temperature can range between 115 and 180°C depending on the feedwater temperature, the cost of incremental heating surface in the economizer, the cost of fuel for the power boiler, the cost of in-house power generation, and the risk for corrosion in downstream equipment.

Devices such as feedwater-to-combustion-air or circulating-water-to-combustion-air heat exchangers operating in conjuction with economizer heating surfaces can often be justified when all factors are considered. These devices have the added attraction that the gas exit temperature can be controlled at low boiler loads to limit corrosion in downstream equipment. Flue gas temperatures as low as 150°C at design load are quite common in countries where fossil fuel is expensive, and 115°C has been employed on one unit in Sweden.

The optimization calculations to ascertain the fuel savings should be reasonably sophisticated, and should preferably employ a method of analysis such as the computerized load-duration-curve approach which Sandwell has developed in recent years. The method should consider the varying efficiency of the turbine generator with load, and the annual operating characteristics of both the recovery and power boilers, with particular regard to the fuels which are fired in the power boiler over its operating range.

ELT SPOUTS

ne design of smelt spout hoods varies from the large common hood to the individual mini- ods offered by Götaverken. The advantages claimed for the mini-hood are , no washing the hood, less rodding of the smelt spouts, less air infiltration into the dissolving tank d hence a smaller quantity to be evacuated, and better access to the spouts for spection, clearing and substitution.

e angle of the smelt spouts varies quite considerably from manufacturer to anufacturer. Reason suggests however, that there will be a smaller variation in the smelt ajectory between high and low smelt flows if the spouts have a steep angle. There will be ss likelihood of impingement of the smelt stream on the wall of the tank or the hood if e spout angle is steep.

DUCED DRAFT FANS AND ELECTROSTATIC PRECIPITATORS

rth American practice normally would employ one double-inlet fan with backward- clined airfoil blades, hydraulic coupling and AC electric motor, independent of the pacity of the boiler or the number of electrostatic precipitators. Scandinavian practice uld normally use two single-inlet induced draft fans with straight radial blades for in-chamber electrostatic precipitators, and would use three fans for three-chamber ecipitators; these single-inlet fans would probably be driven by a variable- eed, DC electric motor. The margins on volume and pressure vary slightly depending on e manufacturer or client preferences, but are of the same order in North America and andinavia. The number of electrostatic precipitators is determined by the emission quirements.

ere is a considerable prejudice against single-inlet fans in North America, and the words verhung wheel" and "thrust bearing problems", have unpleasant undertones in discussions this subject. However, almost every black liquor boiler installed by the several andinavian manufacturers employs single-inlet induced draught fans, and these fans have proven record of continuous operation for up to 16 months in some cases. The straight, dial, blade design contributes greatly to their ability to remain clean, and it is interesting note that these fans do not normally have any nozzles for cleaning-steam or air on the housing, contrary to North American practice.

must not be inferred that the double-inlet fan is an unreliable device, but only that the gle-inlet fan is at least as reliable. Records at one Canadian mill indicated that only r days were lost in the course of 11 years operation due to ID fan problems. Even with s excellent record of availability the higher cost of a twin-fan installation is easily stified because the boiler can be kept in operation at a load of 65 to 80 percent depending the fan margin, with only one fan in operation, whereas a fan, or fan drive, failure in a gle-fan installation will shut down the unit (and the entire mill in a single-boiler tallation) after the liquor storage tank capacity has been reached. The additional cost twin single-inlet fans is somewhat offset by the savings in the cost of the inlet flues.

ncern for air infiltration into electrostatic precipitators, leading to local corrosion, has occasion prompted the location of the ID fan upstream of the precipitator to provide essurized operation of the precipitator and thus eliminate air infiltration. This practice not to be recommended, as the increased fouling which will occur in the ID fan in the rty" location may be severe enough to disrupt boiler operation. The better design proach is to locate the fan in the "clean" location, downstream of the precipitator, and ensure that high-quality expansion joints, seals, casings, and rotary valves are purchased precipitators.

FORCED DRAFT FANS

Although lower first cost supports the single-FD-fan approach, separate fans for primary, secondary, and tertiary air, provide lower operating costs and, more importantly, eliminate the interaction of adjustments between air registers, and contribute to lower TRS emissions and more stable furnace operation.

Again, in North America, the double-inlet fan is used almost exclusively, but the single-inlet fan is generally employed in Scandinavia, and gives lower ductwork costs where suction ducts are drawn to the upper regions of the boiler house for maximum heat recovery and improved ventilation. These suction ducts can with advantage be circular, in which case they require no stiffening, and can incorporate energy-efficient venturis for individual air measurement.

AIRHEATERS

Both steam-to-air and water-to-air heaters have been well proven in operation throughout the world, but the choice of one or other is made more on the basis of client preference and local custom, rather than on a rational investigation of the economics of the one or the other. Such an investigation should be made on the basis of the anticipated annual load duration curve profile, as outlined earlier, particularly if co-generation applies.

Combustion air temperatures have traditionally been 150°C, but, more recently, primary air temperatures of 225°C have been offered. The higher temperature primary air is reported to increase reduction rates to some extent, and to provide more stable furnace operation, particularly with lower-than-normal liquor heating values or solids contents. The advent of the automatic rodding device for primary air ports has meant that the higher air temperature could be adopted with no attendant increase in operator discomfort which would otherwise occur during manual rodding.

RECOVERY BOILER HOUSE ENVIRONMENT

The working environment in modern recovery boiler installations can be greatly improved for the operators by providing good lighting, well-designed stairs and galleries, colourful cladding on boiler and ancillary equipment, an adequate budget for housekeeping, and thus encouraging a pride in the work-place. Safety is improved and it would be reasonable to assume that plant availability, absenteeism, and operator-turnover are also improved.

CONCLUSIONS

A paper of this nature can obviously only include a limited number of points for discussion but the main, and self-evident, conclusions that can be drawn from the above discussion are that the design of a modern recovery boiler is complex, and further, that an increasing degree of sophistication is required in the optimization and selection of both the basic parameters, such as flue gas exit temperatures, and of the components of the plant, such as steam-or-water airheaters.

so, working as a consultant as I do, it is easy to see that boiler manufacturers often erate from deeply-entrenched design standpoints which are stubbornly defended long ter the position has been shown to be untenable because of proven design improvements ade by other manufacturers. The design features, or non-features, which can withstand rutiny, and which would be incorporated in the ideal recovery boiler, in my opinion, would clude:

- An amply-dimensioned furnace .
- Composite tubes in the lower furnace
- Steeply-sloping smelt spouts with mini-hoods
- The elimination of the water-cooled screen
- Widely-spaced platen superheater
- Fully-welded, interstage, indirect-type, attemperator
- The elimination of complex tube screens between superheater and boiler generating bank
- Side-to-side tube spacings of at least 200 mm between centres at the inlet of the boiler generating bank where temperatures greater than 600°C may apply
- Fully-welded generating bank, or in cases of pressures above about 6 MPa, the radiant configuration
- Substantial circulation margins for furnace and generating bank
- Long-flow, non-baffled economizer
- Dry-ash removal from full-width hoppers and precipitator
- Twin ID fans - preferably with straight radial blades and single-inlet design
- Separate FD fans for primary, secondary and, if required, tertiary air.

nally, the use of flue gas tempering from the precipitator outlet to the superheater inlet uld be considered for control of flue gas temperatures and fouling of heating surfaces.

TERATURE CITED

MacCallum, C., "Recovery Boiler Design - The Steam-cooled Screen", TAPPI, Vol. 60, No. 9, September 1977.

MacCallum, C., "The Radiant Recovery Boiler" presented at BLRBAC, Atlanta, Ga., U.S.A., April 1981, also at Canadian Pulp and Paper Association Western Branch Meeting, Harrison Hot Springs, B.C., Canada, May 1981, and a synopsis was published in TAPPI, December 1980.

ST OF FIGURES

VAPOR PRESSURE OF BLACK LIQUOR AT HIGH SOLIDS CONTENTS

by

D.T. Clay, Research Associate
T.M. Grace, Senior Research Associate
The Institute of Paper Chemistry, Appleton, Wisconsin, USA

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

B1 - 1

VAPOR PRESSURE OF BLACK LIQUOR AT HIGH SOLIDS CONTENTS

D. T. Clay, Research Associate
T. M. Grace, Senior Research Associate

The Institute of Paper Chemistry, Appleton, WI 54912

ABSTRACT

A review of existing data on the vapor pressure of black liquor at solids contents above 50% and of techniques for making such measurements was carried out. A method was developed for direct measurement of the boiling point rise of high solids liquors using immiscible carrier oils of relatively low volatility. Black liquor boiling point rise data obtained with this technique up to 90% solids appear to be in general agreement with other limited data that have been published. However, tests on known inorganic solutions have yielded measured boiling point rises that are generally higher than expected. The reasons for this are not known at present.

INTRODUCTION

There appears to be a trend developing toward firing black liquor in recovery boilers at increasingly higher solids contents. An important factor in the technology for producing black liquor at solids contents greater than 65-70% is the vapor pressure of the black liquor as a function of temperature and concentration. The vapor pressure curve plays a major role in determining pressure - temperature requirements for evaporative equipment. This behavior is sometimes expressed in terms of the boiling point rise, defined as the difference between the boiling temperature of black liquor and that of pure water at the same pressure (normally one atm.).

Although boiling point rise data have the most direct value in the design of concentration equipment, there are other uses for black liquor water vapor pressure data.

1. Dry black liquor solids are hygroscopic to some extent. Vapor pressure data would specify conditions under which dry solids could be stored.
2. As black liquor is concentrated, the solubility limit of some of the inorganic constituents is exceeded. Since insoluble material would contribute negligibly to the vapor pressure behavior, vapor pressure data might serve to identify the onset of precipitation and possibly the degree of supersaturation.
3. Vapor pressure measurements can provide information on the physical-chemical nature of the black liquor. This includes heats of vaporization (and hence heats of dilution) and identification of phase transitions.

There are numerous problems in measuring the vapor pressure of black liquor. Many are viscosity related. The high viscosity of concentrated black liquor leads to poor flow characteristics and inhibited convective transfer operations. Pronounced gradients of temperature and concentration can exist in the liquor. Vaporization rates are generally low, and the boiling action does not necessarily eliminate inhomogeneities. In principle, vapor pressure is a thermodynamic property of the black liquor and is determined by establishing an equilibrium between a uniform liquid phase and a uniform vapor phase. Factors leading to nonequilibrium include temperature and concentration gradients resulting from hindered flow, liquor superheat due to suppressed nucleate boiling, and delayed inorganic crystallization. Other problems include difficulty in making accurate measurements of solids contents of the liquor and interference by noncondensable gases (such as air trapped or dissolved in the liquor).

APPROACHES

Several methods have been developed for measuring vapor pressure of liquids; they are potentially applicable to black liquor. The simplest is a direct measurement of the boiling point of the liquor. By coupling the boiling vessel to a barostat, a complete vapor pressure-temperature curve can be determined. This method (at atmospheric pressure) is commonly used for measuring boiling point rise of low solids black liquor and was used by Frederick /1/ to get b.p. rise data up to about 65% solids content. The basic problem is to eliminate superheat in the boiling liquid. For accurate work special apparatuses, which provide for liquid-vapor equilibrium at the temperature sensor, are used. With high solids black liquor, the high viscosity leads to pronounced temperature gradients in the liquor. It is doubtful if this technique can be applied to black liquor beyond about 65-70% solids.

Vapor pressure can be measured directly by placing a vessel containing the quor and a connecting pressure sensor (such as a manometer) in a constant temrature environment. This method was employed by Funk /2/, who used a mercury nometer for pressure sensing and an air hot box for temperature control. Funk had eat difficulty in obtaining good data because of sealing problems associated with tended times at high temperature. A subsequent error analysis of this approach s indicated that the pressure measurement needs to be accurate within 1% of the tual value and the temperature accurate within 0.3°C. The required accuracy and ability in the temperature are beyond the capability of the air hot box used. rect vapor pressure measurements are very sensitive to error from noncondensable ses, since these will contribute to the total pressure measurement. Although ese problems can be minimized by cycling through a number of evacuations and asurements, the persistence with which air can be held in black liquor and the ssible release of other volatiles leave noncondensables as a serious potential oblem.

One technique that has been successfully used to concentrate black liquor l the way to dryness is to use an immiscible liquid (oil) as a carrier for the ack liquor /7/. A similar approach can be used for vapor pressure measurements. e measurement is carried out by placing a refluxing condenser above a pot conining the boiling black liquor and oil. The system operates at atmospheric essure. One temperature sensor measures the boiling temperature (T_B) in the pot d another measures the temperature (T_C) of the refluxing condensate which is uilibrated with the rising vapor. This method is potentially operable all the way to dry solids and is insensitive to the presence of noncondensable gases.

The theory behind this approach is as follows. If two volatile immiscible iquids are equilibrated with a vapor phase, the total pressure of the vapor will be e sum of the vapor pressures of the two liquids. Thus, in the pot,

---

$$P_T = P_{BL}\ (T_B) + P_o\ (T_B)$$

where P_T is the total pressure in the system.

P_{BL} (T) is the vapor pressure of black liquor at temperature T, and P_o (T) is the vapor pressure of the oil at T. In the refluxing condenser the pressure is given by

$$P_T = P_W\ (T_C) + P_o\ (T_c)$$

where P_W (T) is the vapor pressure of water at T. Combining these gives

$$P_{BL}\ (T_B) = P_W\ (T_C) + P_o\ (T_c) - P_o\ (T_B)$$

For oils of relatively low volatility, the difference in the vapor pressure of the oil at the two different temperatures is small compared with the vapor pressure of the water, and the relation simplifies to

$$P_{BL}\ (T_B) = P_W\ (T_c)$$

In this case, the measured temperature difference, $T_B - T_c$, can be identified with the boiling point rise of the black liquor.

Isopiestic methods are another approach. If vessels containing two different solutions are placed side by side in a closed space, vapor will distill from the higher vapor pressure solution to the lower one. At equilibrium, the vapor pressures of each will be equal. If the vapor pressure of one solution is known as a function of concentration and temperature, the other is then determined. This approach is insensitive to the presence of noncondensable gases (although they may increase equilibration time) and total pressure. It requires only a measurement of the equilibration temperature and the concentrations. This approach has the potential ır giving very accurate data. However, equilibration periods can exceed 24 hours, ıd the development of special apparatus is required.

ISTING DATA

Black liquor boiling point rise data from six different sources are given ı Figure 1. Since different liquors were used in these studies, only general com- ırisons can be made. TAPPI Monograph 32 is a widely used source of boiling point ıse data, especially for lower solids liquor. This curve was developed by Han /3/ ıd is based heavily on neutral sulfite liquors. Han found close agreement with ıree kraft black liquor (western hemlock) points as measured by Kobe /4/. This led ın to suggest that the entire curve is applicable to kraft liquors. Kobe's experi- ıntal approach was to boil the liquor under various reduced pressures and measure ıquor temperature, condensing vapor temperature and system pressure. Recently ıederick /1/ published b.p. rise data determined by a similar technique (but at ımospheric pressure) at solids contents up to 65% Arhippainen /5/ reported b.p. ıse data for Finnish pine kraft black liquor. Although the experimental approach ıs not described, it was probably similar to the above.

A boiling point rise value for 80% solids black liquor is implied within ıe process specifications for a high solids, thin-film evaporator described by drews /6/. This is a best fit value from data generated in various bench and ıall pilot scale apparatus. Subsequently, an additional point at 88% solids was ıtained from the same source.

Clay /7/ reported b.p. rise values for black liquors up to 97% solids. The ıperimental approach was to measure liquid and vapor temperatures under pressure in e presence of a low volatile oil. The oil was used to enhance system fluidity. is allowed b.p. rise data to be obtained at solids levels above 90%.

Funk /2/ measured the vapor pressure of black liquor directly at various solids levels and calculated b.p. rise values from the vapor pressure vs. temperature curves. Long times (more than 24 hours) were involved to allow static equilibrium to be obtained. These data deviate considerably from the general trends exhibited by all of the other data. It is possible that this is because the long times involved allowed inorganic precipitation to proceed to completion. However, there are serious questions concerning the validity of these data because of leakage problems and complications from noncondensable gases.

With this exception, all data in Figure 1 show a continuous accelerating increase in b.p. rise as solids increase. There is very good agreement between the data of Clay and those of Andrews at solids levels above 70%. Extrapolation of Frederick's and Kobe's data would seem to be consistent with these trends. Clay's data appear high at solids levels below about 65%. The significance of this will be discussed later.

EXPERIMENTAL APPROACH

The present study determined boiling point rise directly based on dynamic steady-state temperature measurements. Oils of different volatility were used to enhance fluidity and cover a range of water vapor pressure. All of the data were collected at atmospheric pressure. The assumption that the black liquor-oil system is immiscible was confirmed by experimental experience. As was discussed earlier, the measured boiling and condensing temperatures are a direct measure of the boiling point rise of the black liquor as long as the oils are relatively nonvolatile. With high volatility oils, the measured temperatures will underestimate the correct b.p. rise of the liquor.

The experimental apparatus is shown in Figure 2. The vessel has a volume 3.7 liters. The agitator speed was on the order of 100 rpm. The entire vessel s submerged in a temperature controlled oil bath. Two thermocouples were immersed the liquid phase just above the agitator. The condensing temperature was asured by a thermocouple positioned in an uninsulated glass "Y" section immediate- above the level of the oil in the bath. The thermocouples were connected to a gital readout sensitive to 0.06°C (0.1°F). The thermocouples and readout were librated against a standard National Bureau of Standards thermometer. The conden- te bypass return or removal point was immediately above the "Y" section. A water oled glass condenser, vented to a water manometer open to the atmosphere, was ed. During startup, noncondensables are vented to the atmosphere through a valve cated between the condenser and manometer.

The following data were recorded.

1. Two temperatures of the liquid phase in the vessel
2. Condensing temperature in the "Y"
3. Atmospheric pressure (mercury barometer)
4. System differential pressure (water manometer)
5. Visual observation of condensation
6. Oil bath temperature
7. Condenser top vent temperature

e initial solids in the black liquor were measured by an extended surface oven- ying procedure. Intermediate solids were calculated based on the total liquor arged and the amount of condensate removed.

Observations

The presence of the oil in with the black liquor led to some unusual behavior. It was possible to obtain up to 6°C superheat in the liquid when vigorous boiling occurred. This was noted for both black liquor and standard salt solutions. Higher superheats were found with higher solids contents and were not affected by agitator speed. Both liquid phase temperature readings were consistently in agreement.

The temperature recorded in the "Y" section varied considerably, corresponding to contact with superheated vapor, saturated condensing vapors, subcooled condensate and hot noncondensable gases. With vigorous boiling, superheated vapors were present. Mild boiling gave the saturated condensed vapor. Low or no boiling gave the latter two conditions. The immiscibility of the water and oil was clearly seen in the condensate for all runs.

Black liquor solids contents greater than 90% were not obtained in this system. Somewhere between 85 to 90% solids the system became viscous enough that a safety key in the agitator drive system sheared. The resulting liquor was a tarlike mass that quickly hardened on cooling and separated from the oil. A modified procedure and agitator design should allow for measurements at 90% solids or greater.

The liquid phase temperature recorded when the presence of condensate was just lost in the "Y" was used for determining b.p. rise. Occurring simultaneously with the loss of condensate was an increase in system vacuum and a rapid decay in vapor temperature. Typically the exterior oil bath temperature was within 2°C of the liquid phase temperature so that temperature gradients in the liquid should be minimal.

Vapor temperature values most consistent with calculated dew points for the water/oil systems occurred when condensing occurred only in the "Y" section. When

ndensation extended into the condenser, superheated vapor gave high measured tem-
ratures. Superheats of 3 to 6°C were measured during vigorous boiling.

The critical conditions for vapor and liquid temperature measurements did
t occur at the same time. For this analysis the liquid temperature used for
lculating b.p. rise was that measured when condensing was first lost. The vapor
mperature used was that calculated from the known water and oil vapor pressure vs.
mperature relations.

ocedure

The vessel was typically charged with 400 g of black liquor and 750 g of
l and placed in the oil bath. The bath temperature was increased until vigorous
iling occurred in the system. The vent valve was opened to purge noncondensables
til condensing occurred in the "Y." After condensing had extended into the con-
nser, the bath temperature was slowly reduced. Data were taken periodically during
is cooling step. As the system cooled, the saturation temperature was reached
the "Y." This temperature was generally more stable than under superheat or sub-
oled conditions. The liquid phase temperature continued to decrease slowly during
is period. As cooling continued, the vapor temperature dropped suddenly,
gnaling loss of condensate. This was always checked visually. The liquid phase
lue would then stabilize, and this was taken as the boiling temperature for the
p. rise calculation.

Higher solids were produced by increasing the bath temperature and
thdrawing condensate after the system had a positive pressure and condensing was
curring again. A measured amount of condensate was withdrawn. Any oil which
rried over was returned to the vessel. The cooling cycle was reinitiated to

obtain the desired boiling temperature. This sequence was repeated to generate successively higher solids contents.

The oils used included hexadecane, dodecane, and decane. All of these are less volatile than water. The black liquor was obtained from Thilmany Pulp & Paper Co. and had an initial solids content of 42.8%. In addition, aqueous NaOH and NaCl solutions were used to check out the system.

EXPERIMENTAL RESULTS

Initial tests were carried out with NaOH and NaCl solutions. A check on the accuracy of the results obtained was complicated by a divergency in published data on the vapor pressure of these solutions. However, the measured values of boiling point rise were generally above the range of values expected on the basis of published data. These results are shown in Figures 3 and 4. In all cases b.p. rises are slightly higher in runs where oil was used than for just the aqueous solutions. For NaOH, deviations from published data increase with increasing NaOH concentration. For the NaCl solutions, the deviation from expected behavior is greatest with oil present and with lower NaCl concentrations. The reason for this behavior is not known at present.

Measured values of b.p. rise for the black liquor are shown in Figure 5. In general, these data agree in magnitude and shape with the other published data on black liquor shown in Figure 1. This is especially true at the higher solids content. At lower solids contents the present black liquor data seem to be flattening out at higher values, and in such a way that it appears the data would not extrapolate back to zero b.p. rise at infinite dilution. This is very similar to the behavior observed with the NaCl solutions.

The present black liquor data show the accelerated increase in b.p. rise ith increasing solids content found by Andrews and by Clay and suggested by ederick's data and those of Kobe. This is in marked contrast to the results of Funk d Grace in which there was a pronounced flattening of the b.p. rise at higher lids, which was attributed to crystallization of inorganic salts. The prepon- erance of the evidence suggests there are problems with Funk's data, although this s not been definitively shown.

It is obvious that the present technique also has problems. The deviation the NaCl solution data from published values, especially at lower solids con- ents, and the trend in the black liquor data (to extrapolate to a finite b.p. rise 0% solids) are disturbing. Work is continuing toward understanding and over- ming these problems.

NCLUSIONS

A technique has been developed which is capable of giving b.p. rise data on ack liquor at solids contents approaching 90%. There are some problems which lead erroneously high values of b.p. rise which remain to be resolved. However, the viations between measured and true values are probably no more than a few °C.

The data show an accelerated increase in the b.p. rise of black liquor at lids contents greater than about 70%, in agreement with most published data. The iling point rise in ultra high solids liquor may approach or even exceed 50°C. is is in marked contrast to the results of Funk and Grace. Those data must now be nsidered suspect.

It would be useful to have precise vapor pressure data obtained under atic equilibrium conditions as a reference for checking more rapid techniques for

measuring b.p. rise. Isopiestic methods show promise for giving such results and should be investigated.

REFERENCES

1. Frederick, W. J., Sachs, D. G., Grady, H. J., and Grace, T. M. Boiling point elevation and solubility limit for black liquors. Tappi 63(4):151(April, 1980).
2. Grace, T. M. and Funk, M. S. Vapor pressure of black liquor. International conference on recovery of pulping chemicals, Vancouver, B.C., Sept. 22-25, 1981.
3. Han, S. T. Physical properties of neutral sulfite spent liquors. Tappi 40 (11):921(Nov., 1957).
4. Kobe, K. A. and Sorenson, A. J. Specific heats and boiling temperature of sulfate and soda black liquor. Pacific Pulp & Paper Ind. 13(2):12(1939).
5. Arhippainen, B. and Jungerstam, B. Operating experience of black liquor evaporation to high dry solids content. Tappi 52(6):1095-9(June, 1969).
6. Andrews, R. S. and Roscoe, R. W. Thin-film evaporation of black liquor to high solids. Tappi 64(12):49-51(Dec., 1981).
7. Clay, D. T. and Karnofski, M. A. Black liquor solid formation during oil-flash evaporation. Tappi 64(12):45-8(Dec., 1981).

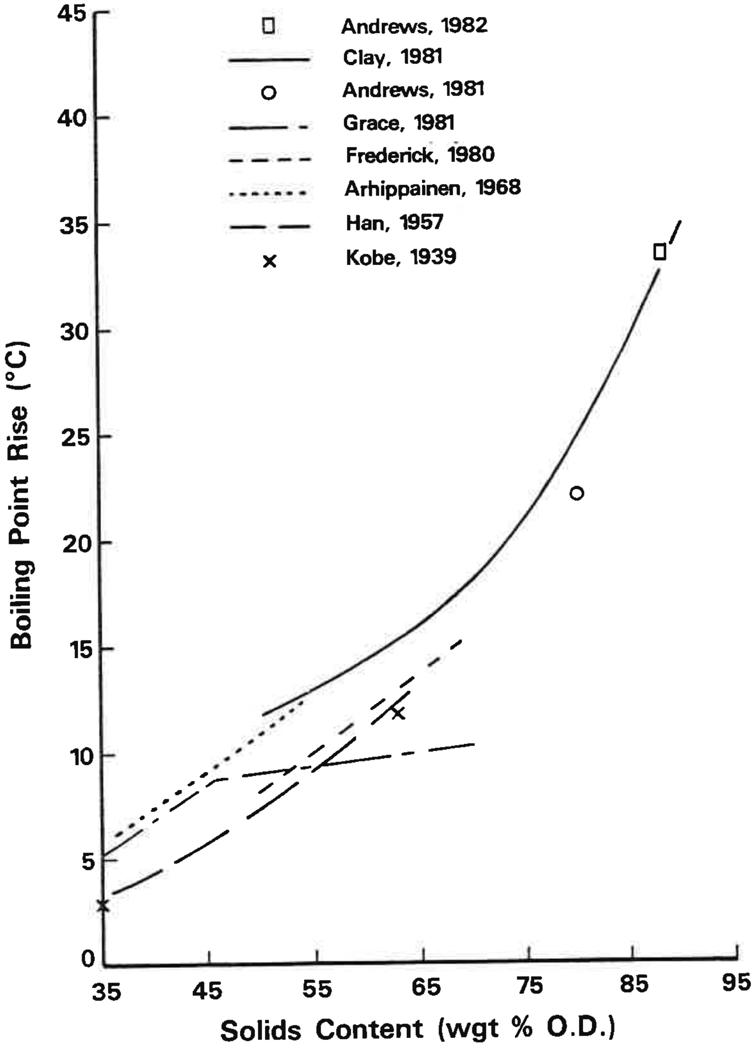
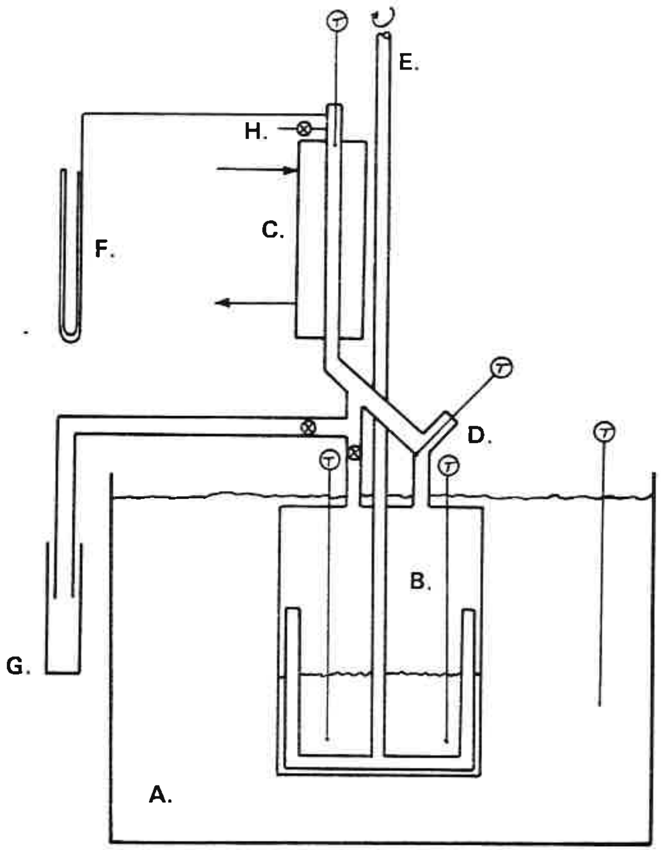


Figure 1. Kraft liquor boiling point rise data from several sources.



A. Temperature controlled oil bath.
B. 3.7 liter vessel.
C. Water cooled condenser.
D. Y ambient cooked condensing section.
E. Agitator.
F. Water manometer.
G. Collection of condensed Condensate.
H. Noncondensible vent.

Figure 2. Boiling point rise experimental apparatus.

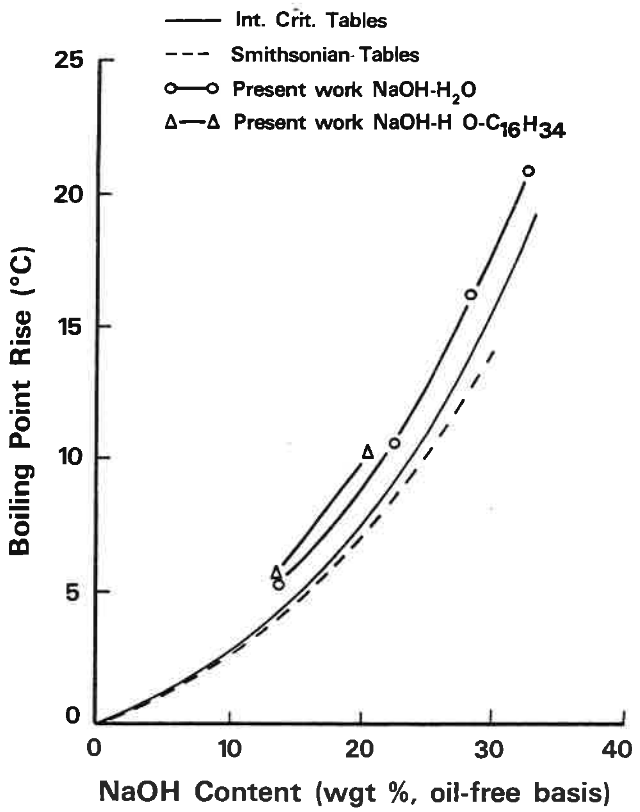


Figure 3. Sodium hydroxide boiling point rise data.

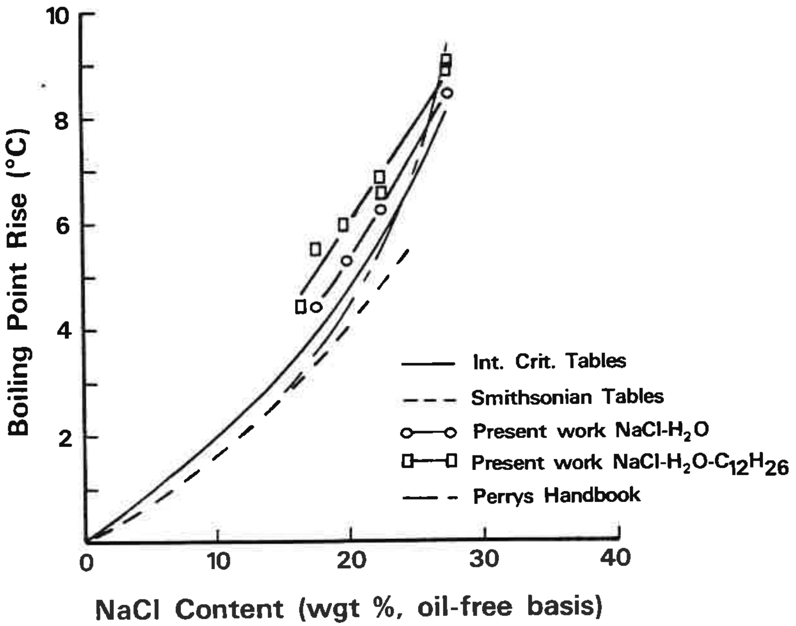


Figure 4. Sodium chloride boiling point rise data.

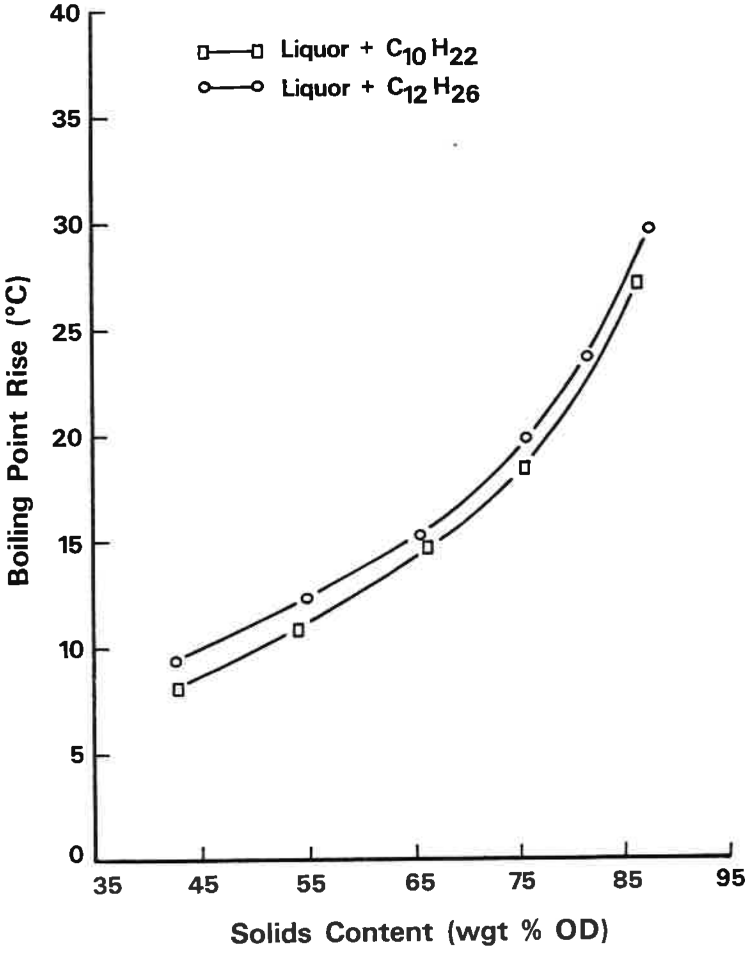


Figure 5. Kraft liquor boiling point rise - present work,

RECENT DEVELOPMENTS IN BLACK LIQUOR ANALYSIS

by

L. Söderhjelm, Research Manager
U. Koivuniemi, Deputy Research Manager
The Finnish Pulp and Paper Research Institute, Helsinki, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

RECENT DEVELOPMENTS IN BLACK LIQUOR ANALYSIS

Liva Söderhjelm, Research Manager
Unto Koivuniemi, Deputy Research Manager
The Finnish Pulp and Paper Research Institute, Helsinki, Finland

1 Introduction

There seems to be a demand for new methods for analysing sulphate black liquor throughout the pulp-making world. We no longer have time for gravimetric manipulation or many hours of wet oxidation. We want the analyses to give a better description of the liquor, to be more accurate and to be easier to perform than before. Some recent improvements in this area are:

- Rapid determination of solids by McDonald /7/
- Rapid determination of carbonate by Donetzhuber /3/
- Analysis of rheological properties by Co /2/ and Sandquist /8/.

Further, work is being done to apply ion chromatography to the determination of anions and organic acids in black liquor as well as on the use of automatic devices, based on IR, for the determination of total sulphur.

This paper deals with the analysis of four characteristics:

- calorific values
- surface tension
- foaming properties
- ratio of inorganics to organics.

2 Calorific values

The energy crisis has emphasized the importance of the calorific value of all sorts of compustibles, including black liquor. Calorific value is important in evaluating the fuel value of the liquor and in assessing the liquor producing process. There are new automatic devices on the market for determing calorific value, but the principle is still the same: the sample (together with paraffin oil if wet) is introduced into the autoclave (bomb), oxygen is added, the sample is ignited and the heat evolved is recorded. The amount of energy thus measured per unit mass is the gross calorific value, from which the net calorific value is derived. Since this latter is an intricate step, the following procedure is recommended:

$$W_d = \frac{100}{K} \cdot W \qquad (1)$$

W_d = gross calorific value of dry matter, MJ/kg
K = dry matter content of the sample, %
W = measured heat of combustion per unit mass, MJ/kg

$$W'_d = W_d - W_h - W_s \qquad (2)$$

W'_d = net calorific value of dry matter, MJ/kg
W_h = correction for hydrogen, MJ/kg
W_s = correction for sulphur, MJ/kg

The hydrogen correction has to be made for all combustibles and is due to the fact that water originally present in the sample or formed during combustion condenses in the bomb, whereas it stays vaporized in a furnace. The hydrogen correction is calculated as follows:

$$W_h = \frac{2{,}449 \cdot 18{,}015 \cdot h}{2{,}015 \cdot 100} = 0{,}219 \cdot h \qquad (3)$$

2,449 is the molar heat of evaporation of water
18,015 is the molecular mass of water
2,015 is the molecular mass of hydrogen
h is the percentage of hydrogen in the dry matter.

The sulphur correction is specific for black liquor recovery boilers and is due to the fact that burning the liquor reduces almost all the sulphur to sulphide while it is almost completely oxidized to sulphate in the laboratory bomb. A minor error results because neither of the above mentioned processes is complete. Other inorganic combustion products will also interfere with the result. Detailed information is provided by Gullichsen /6/.

The sulphur correction is obtained from:

$$W_s = \frac{1{,}012 \cdot s \cdot 1000}{32{,}06 \cdot 100} \qquad (4)$$

1,012 is the molar enthalpy of the reaction $Na_2S + 2O_2 \rightarrow Na_2SO_4$
32,06 is the molecular mass of sulphur
s is the percentage of sulphur in the dry substance.

For the calculation of the net calorific value of the sample as such the following formula is applied:

$$W' = \frac{W'_d \cdot K}{100} - 0{,}02449\ (100 - K) \qquad (5)$$

Thus the net calorific value can only be calculated if the hydrogen and sulphur contents of the liquor are known. By introducing correction factors into formula (4) the sulphur correction can be altered to correspond to any degree of reduction in the furnace.

3 Surface tension

Measurements of surface tension of black liquor using a Du Noüy ring-type tensiometer have recently been published by Beckwith et al. /1/ The authors state that "surface tensions could not be measured for solids contents above 45 %, because a tube of liquor was pulled away from the surface". The tensiometer method has several drawbacks: thermostating is difficult, evaporation takes place at the surface and film formation occurs on the surface. To overcome this a stalagmometric method has been developed. The device is shown in fig. 1; it is constructed of glass and is vapour tight.

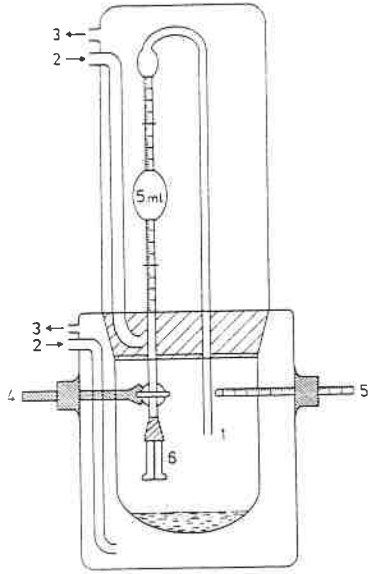


Fig. 1. Stalagmometer for the determination of the surface tension of black liquor.
1 = vacuum connection
2,3 = water inlets and outlets to the thermostat
4 = flow regulation valve
5 = thermometer
6 = interchangeable capillary tip

The sample is introduced into the capillary tube by suction. The valve is regulated to give a steady flow of droplets and the number of drops is counted. The same procedure is repeated with a liquid of known surface tension.

The result is calculated from the formula:

$$\sigma_1 = \frac{n_2}{n_1} \cdot \frac{\rho_1}{\rho_2} \sigma_2$$

σ_1 and σ_2 are the surface tension values of the sample and the calibration value respectively

n_1 and n_2 are the numbers of drops

ρ_1 and ρ_2 are the densities

It is important that the surface tension of the calibration liquid is close to that of the sample. For black liquor measurements acetic acid has been used as calibration liquid.

The rate of flow must be carefully chosen and a sufficiently long drop formation time allowed for. Equilibrium must be reached within the drops. The relationship between drop formation time and surface tension values is shown in fig. 2. We believe that this phenomenon is due to the slow formation of the drops' surface: several seconds is needed for the surfactants (probably tall oil soap) to travel from within the droplets to their surface. The higher the viscosity the longer is the time needed to reach equilibrium.

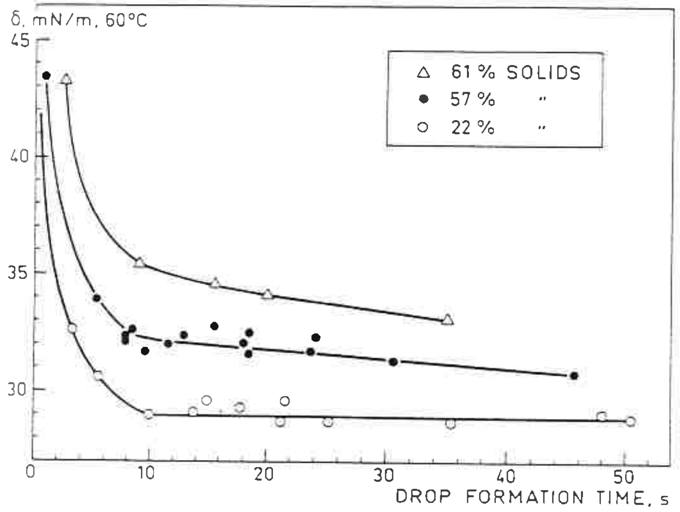


Fig. 2. Influence of drop formation time on surface tension values obtained.

Figs. 3, 4 and 5 show surface tension values obtained for Finnish black liquor from kraft pulping. In fig. 3 it was impossible to obtain accurate values for high solids content because of the high viscosity and poor drop formation. We know, however, that surface tension increases when the dry matter content reaches a certain level. Fig. 4 shows that surface tension decreases with increasing temperature, which is in accordance with findings by others /4/. Again it has been difficult to make accurate measurements in the area where the viscosity is high, i.e. at low temperature. Fig. 5 shows the change in surface tension when crude tall oil soap (skimmings) is added to a liquor of about 16 per cent dry matter content.

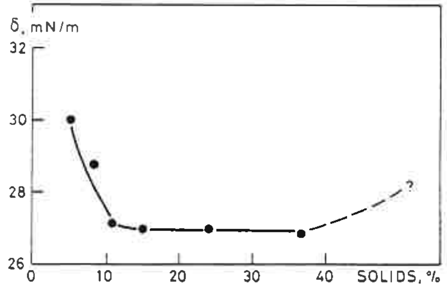


Fig. 3. Surface tension versus solids content at 60°C.

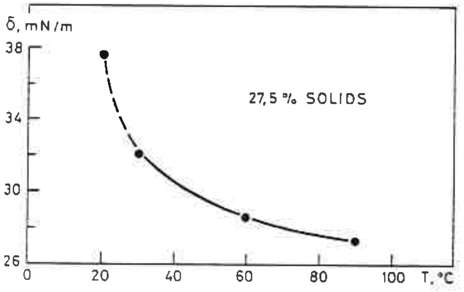


Fig. 4. Surface tension versus temperature.

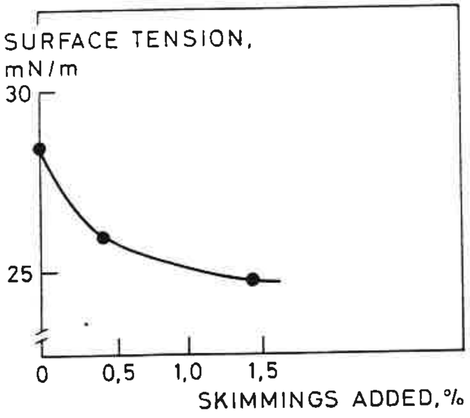


Fig. 5. Changes in surface tension when skimmings are added to a black liquor sample.

4 Foaming properties

Because of the frequent foaming problems encountered in pulp mill flash tanks and in the first stages of evaporation, an investigation was undertaken to find an analytical method for determining the foaming characteristics of black liquor. Most of the methods published so far are concerned with pulp washing and are based on a stream of air being passed through the liquor. In this case we wanted to avoid air and to simulate foam formation under conditions where the gas phase consists of water vapour, methanol, turpentine, etc. Since the dynamic behaviour of the foam is influenced by viscosity, attention was paid to the temperature. We simulated the mill situation by using an autoclave and applying a sudden release of pressure blowing and measuring the amount of foam. The arrangement is shown in fig. 6.

Experiments were performed at different blowing temperatures and different solids contents. Some preliminary results are shown in fig. 7. The curves indicate that foaming reaches a maximum at a certain solids content. This is in accordance with the finding at mills, where foaming is observed to decrease as the solids content increases during evaporation.

The work on foaming characteristics is being continued.

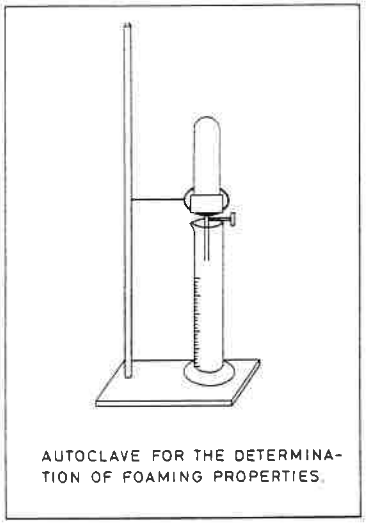


Fig. 6. Arrangement for the measurement of foaminess.

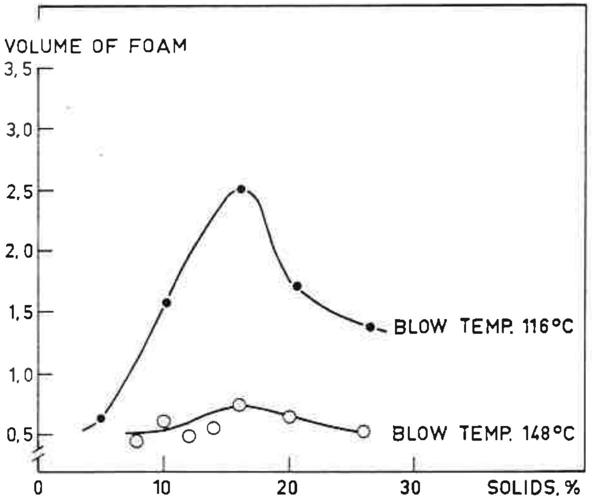


Fig. 7. Foaminess versus solids content at different blow temperatures.

5 Ratio of inorganics to organics

The ratio inorganics/organics in black liquor is often requested when the liquor does not burn properly in the recovery boiler.

Perhaps the ratio would be determined more often if the method were simple, fast and dependable. However, it seems impossible to find a method which fulfils all these demands simultaneously.

Figures which correlate with the inorganics content of the black liquor are easy to obtain using the ash or sulphated ash determinations. However, the results of the ash determination and particularly that of the sulphated ash determination are so much higher than the content of independently determined inorganic compounds that there is some doubt as to whether these figures can be used for the inorganics in black liquor.

The TAPPI method T 625 /10/ recommends that the inorganics of the liquor be determined as sulphated ash and expressed as NaOH. This method gives a rough estimate of the inorganic content and gives results of about the right order.

Opinions differ on what are inorganics and what are organics. The distinction between the two is not always defined in the same way.

The TAPPI method gives all the true inorganic compounds, organically bound sodium and potassium and organically bound sulphur all changed to sulphates and then calculated as NaOH.

Grace et al. /5/ include organically bound sodium but not organically bound sulfur within the category of inorganics.

J. Vila /9/ has studied the correlations between inorganic content and sulphated ash, and between organically bound sodium and total sodium. In his view the inorganics include only the true inorganic content measured by individual analysis and not organically bound sodium or sulphur.

The principle adopted at The Finnish Pulp and Paper Research Institute is close to TAPPI's way of thinking, though the methods are different.

The analyses needed are:
The ash,
The carbonate content of the ash as determined by titration with hydrochloric acid,
The carbonate content of the liquor as determinated by a CO_2 evolution method /3/.

Using the results of these determinations the corrected ash is calculated. The correction term corresponds to the organic carbon, which, during the ashing procedure, has burnt to carbon dioxide and combined with organically bound sodium and also with sodium hydroxide to form Na_2CO_3. In this way, the error caused by the conversion of organic carbon to inorganic carbon is corrected.

The result is calculated using the formula:

$$I = a - (b - c) \tag{7}$$

where

I = percentage of inorganics in the dry solids
a = percentage of ash in the dry solids
b = ash carbonate as percentage of dry solids expressed as CO_3
c = liquor carbonate as percentage of dry solids expressed as CO_3

As an example we have analysed the main inorganic components in a typical black liquor and in the ash of the same liquor. The results are presented in Table 1.

Table 1. Analysis of a black liquor and black liquor ash

	liquor	ash
Dry solids	66,0 %	
In dry solids x)		
ash	48,0 %	
sodium Na	18,1 %	
potassium K	0,45 %	
total sulphur S	5,15 %	4,17 %
carbonate CO_3	3,69 %	17,5 %
hydroxide NaOH	2,20 %	
sulphide Na_2S	5,79 %	not detectable
thiosulphate $Na_2S_2O_3$	2,02 %	" "
sulphite Na_2SO_3	not detectable	" "
sulphate Na_2SO_4	7,31 %	18,3 %
sulphate expressed as sulphur S		4,17 %

x) All the results are calculated on the same basis i.e. as percentage of dry solids.

The figures reveal that the amount of carbonate has increased considerably during the ashing and that the correction according to formula (7) is essential. A slight error is introduced by the unavoidable substraction of the carbonate that has become bound to the sodium hydroxide originally present in the liquor. (The amount corresponding to the hydroxide ion should have been left on the inorganic side). An additional error is the loss of some sulphur compounds during ashing. These imperfections are broadly compensated for by the oxidation of non volatile sulphur compounds to sulphate.

Table 2 presents a comparison between results obtained according to the different principles mentioned earlier.

Table 2. Ratio of inorganics to organics according to different principles.

	Inorganics %	Ratio inorg/org
Inorganic compounds as analyzed including 1,2 % NaCl	26,0	0,35
Ash (temperature raised gradually to 700 °C)	48,0	0,92
Sulphated ash	58,5	1,41
Sulphated ash expressed as NaOH	33,0	0,49
Inorganics according to formula (7)	34,2	0,52
Inorganic compounds as analyzed plus organically bound Na	35,0	0,54
Ibid. plus organically bound sulfur	35,3	0,55

LITERATURE

1. Beckwith, W.F. - Small, J.D. - Wood, D.A.: Surface tension of black liquor. Proc. Int. Conf. Recovery of Pulping Chemicals. Vancouver, 1981, s. 49-51.

2. Co, A. et al.: Viscosity of black liquors at high temperatures. Ibid., s. 57-60.

3. Donetzhuber, A.: Rapid determination of carbonate and inorganic sulphur compounds. To be published.

4. Fòliadova, Z.I. - Kiprianov, A.I.: Physicotechnical properties of black liquors prepared from the pulping of hardwoods. Bum. Prom-st. 1979:11, s. 20.

5. Grace, T.M. et al.: Determination of the inorganic composition alkaline black liquors. TAPPI Vol. 60, No 4 April 1977.

6. Gullichsen, J.: Heat values of pulping spent liquors. Proc. Symp. Recovery of Pulping Chemicals. Helsinki, 1968, s. 211-234.

7. McDonald, K.L.: Rapid determination of kraft black liquor solids. TAPPI 62 (1979):1, s. 80-81.

8. Sandqvist, K.: Rheological properties and evaporation of black liquors at high dry solids content. Int. Conf. Recovery of Pulping Chemicals. Vancouver 1981, s. 267-271.

9. Vila, J.: Fast determination of the inorganic fraction in kraft black liquor. TAPPI Vol. 63, No 11 November 1980.

10. -: Analysis of soda and sulfate black liquor. TAPPI method T 625 ts-64.

RHEOLOGICAL PROPERTIES OF BLACK LIQUORS

by

A. Co, Assistant Professor
M.O. Wight, Graduate Assistant
Department of Chemical Engineering, University of Maine, Orono, Maine, USA

Paper to be presented at the

Black Liquor Recovery boiler symposium 1982, Helsinki, August 31 - September 1, 1982

RHEOLOGICAL PROPERTIES OF BLACK LIQUORS

A. Co, Assistant Professor
M.O. Wight, Graduate Assistant

Department of Chemical Engineering
University of Maine, Orono, Maine, USA

1. Abstract

Linear viscoelastic properties of southern softwood kraft liquors with solids contents ranging from 55% to 75% were examined with the small-amplitude oscillatory shear experiment. Dynamic viscosity and storage modulus data at temperatures ranging from 40°C to 80°C were obtained. Composite curves of these data were constructed by the use of reduced coordinates. A frequency range of three decades was covered. The data indicate that the liquor tested is uncrosslinked and can be treated as a polymeric fluid of low molecular weight.

2. Introduction

There have been recent interests in understanding the rheological properties of black liquors of high solids contents. Kim et al. (1981), Wight et al. (1981) and Co et al. (1982) reported the viscosity curves for various liquors of high solids contents over wide ranges of shear rates and temperatures. They observed Newtonian behavior at low shear rates and shear thinning behavior at high shear rates. In this study the linear viscoelastic properties of black liquors of high solids contents were examined using the small-amplitude oscillatory shear experiment. The results of this work will shed some light on the structural characteristics of the liquors.

3. Small-Amplitude Oscillatory Shear Flow

The small-amplitude oscillatory shear experiment is often used to characterize viscoelastic materials (Bird et al., 1977; Ferry, 1980). This type of flow experiment can be performed with a cone-and-plate geometry or a parallel-disk configuration.

3.1 The Cone-and-Plate Instrument

As shown in Figure 1, the cone is oscillated at a frequency ω with a small strain amplitude. The torque $\mathcal{T}$ required to hold the lower disk stationary is measured. In our study we used a cone of 2.5 cm radius with a 0.040 radian (2.3°) cone angle.

With a small strain amplitude, the torque $\mathcal{T}$ (response) oscillates with the same frequency as the angular displacement ϕ of the cone. For an angular displacement given by

$$\phi = \phi^\circ \sin \omega t \qquad (1)$$

the torque response will be

$$\mathcal{T} = \mathcal{T}^\circ \sin (\omega t + \varphi) \qquad (2)$$

where φ is the phase shift, and ϕ° and $\mathcal{T}^\circ$ are the amplitudes of the angular displacement and torque, respectively. From the out-of-phase response of the torque $\mathcal{T}$ one can calculate the material function η', i.e.,

$$\eta' = 3\mathcal{T}^\circ \vartheta_0 \sin \varphi / 2\pi R^3 \phi^\circ \omega \qquad (3)$$

The in-phase response gives the material function η'', in which

$$\eta'' = 3\mathcal{T}^\circ \vartheta_0 \cos \varphi / 2\pi R^3 \phi^\circ \omega \qquad (4)$$

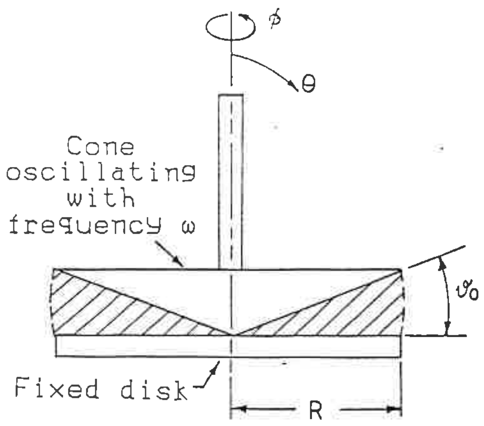


Figure 1. The Cone-and-Plate Instrument

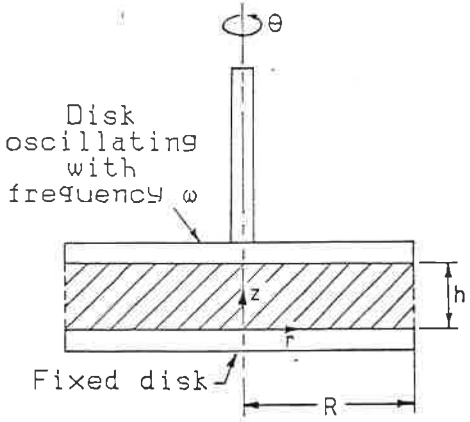


Figure 2. The Parallel-Disk Instrument

The dynamic viscosity $\eta'(\omega)$ may be thought of as the viscous contribution associated with energy dissipation; $\eta''(\omega)$ may be thought of as the elastic contribution associated with energy storage. For Newtonian fluids, $\eta'=\mu$ (viscosity) and $\eta''=0$.

The elastic contribution is also reported as the "storage modulus" G', in which $G'=\omega\eta''$; and the viscous contribution as the "loss modulus" G'', in which $G''=\omega\eta'$.

3.2 The Parallel-Disk Instrument

The parallel-disk instrument, shown in Figure 2, has the upper disk oscillating at a frequency ω with a small strain amplitude. From the angular displacement θ and the torque response $\mathcal{T}$, one can calculate the material functions:

$$\eta'=G''/\omega = (\mathcal{T}^\circ h \sin\varphi/2\pi R^4\theta^\circ\omega)[3 + d\log(\mathcal{T}^\circ \sin\varphi/2\pi R^3)/d\log(R\theta^\circ\omega/h)] \quad (5)$$

$$\eta''=G'/\omega = (\mathcal{T}^\circ h \cos\varphi/2\pi R^4\theta^\circ\omega)[3 + d\log(\mathcal{T}^\circ \cos\varphi/2\pi R^3)/d\log(R\theta^\circ\omega/h)] \quad (6)$$

where φ is the phase shift, and θ° and $\mathcal{T}^\circ$ are the amplitudes of the angular displacement and torque, respectively. Derivations of Eqs. 3 to 6 can be found in Wight (1982).

4. Experimental

The Rheometrics Mechanical Spectrometer (model RMS 7200) was used in this study. The sinusoidal angular displacement of the cone or upper disk was generated by a Tektronix FG 501 function generator, which drove the torque motor of the RMS. A transducer mounted underneath the lower disk measured the torque. The RMS was interfaced with a Digital PDP 11/60 computer to aid in data acquisition and analysis.

The testing assembly was enclosed in an environmental chamber for temperature and humidity control. The environmental chamber was similar to the one used by Wight et al. (1981). The humidity level in the chamber was controlled to maintain the moisture content of the sample during the experiments.

The samples studied were mill kraft liquors made from southern softwood. Each sample was concentrated to the desired solids content using an evaporating unit equipped with a nitrogen gas blanket to prevent further oxidation of the liquor. The solids contents of the liquors were determined following a modification by Co et al. (1982) of the procedures of McDonald (1979) and Kemeny and Chagin (1973).

5. Discussion of Results

The linear viscoelastic characteristics of southern softwood kraft liquors with solids contents ranging from 55% to 75% were investigated in small-amplitude oscillatory shear flow. Measurements from cone-and-plate and parallel-disk geometries were in fair agreement (within ± 5%). The experiments were confirmed to be in the linear viscoelastic regime by using different amplitudes of angular displacement, rangine from 0.004 to 0.04 radian.

For uncrosslinked polymers of low molecular weight, composite curves of the viscoelastic functions at various temperatures can be plotted by using the reduced coordinates (Ferry, 1980):

$$\eta'\eta_{oo}/\eta_o \quad \text{vs.} \quad \omega\eta_o T_o\rho_o/\eta_{oo}T\rho \qquad (7)$$

$$G'T_o\rho_o/T\rho \quad \text{vs.} \quad \omega\eta_o T_o\rho_o/\eta_{oo}T\rho \qquad (8)$$

where η_o is the zero-shear-rate viscosity, ρ is the density, and the additional subscript o refers to the reference temperature T_o. The data in this study were plotted using these reduced coordinates and assuming that the density remained essentially constant in the temperature range investigated. Examples of these plots are shown in Figures 3 to 6. Additional plots can be found in Wight (1982).

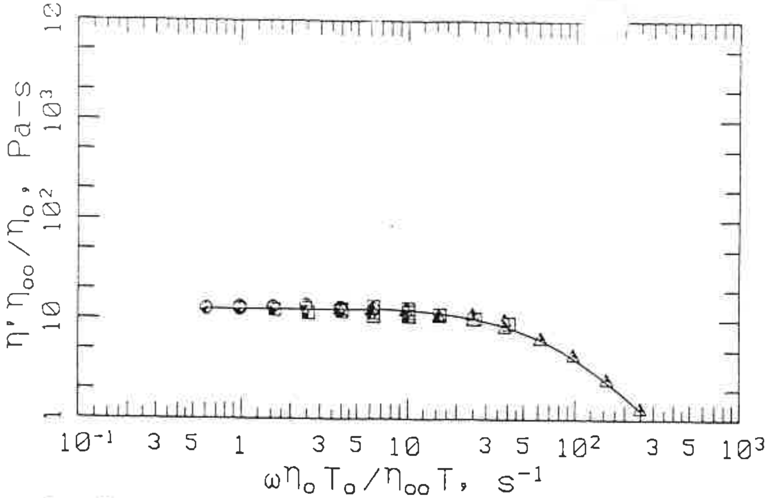


Figure 3. · Dependence of reduced dynamic viscosity on reduced frequency for liquor of 65% solids at various temperatures: the triangles are for 40°C, η_o=77 Pa-s; the squares are for 50°C, η_o=13.0 Pa-s; and the circles are for 70°C, η_o=1.33 Pa-s. The reference temperature is 50°C.

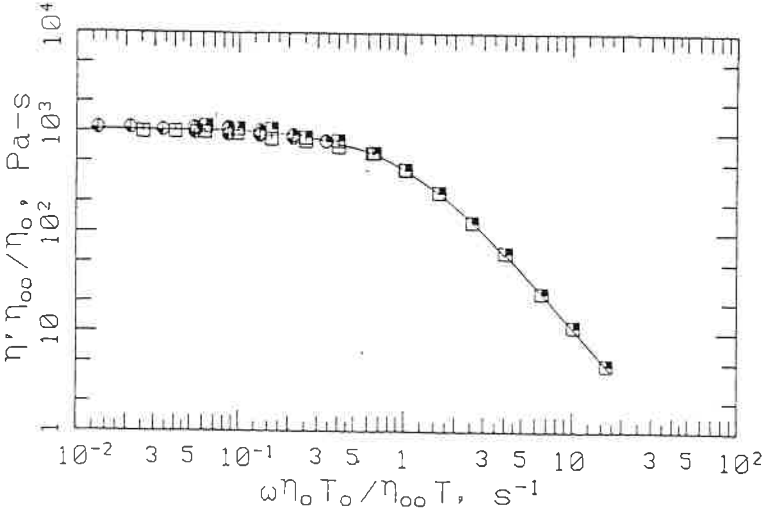


Figure 4. Dependence of reduced dynamic viscosity on reduced frequency for liquor of 75% solids at various temperatures: the squares are for 50°C, η_o=1100 Pa-s; and the circles are for 80°C, η_o=10 Pa-s. The reference temperature is 50°C.

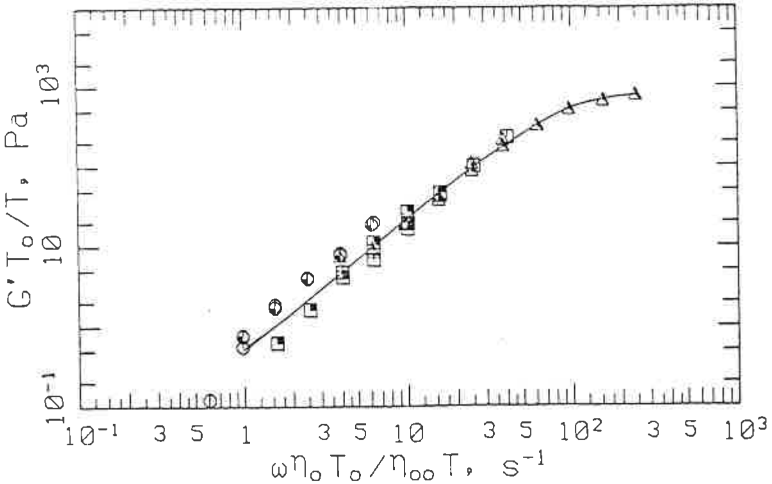


Figure 5. Dependence of reduced storage modulus on reduced frequency for liquor of 65% solids at various temperatures: the triangles are for 40°C, η_o=77 Pa-s; the squares are for 50°C, η_o=13.0 Pa-s; and the circles are for 70°C, η_o=1.33 Pa-s. The reference temperature is 50°C.

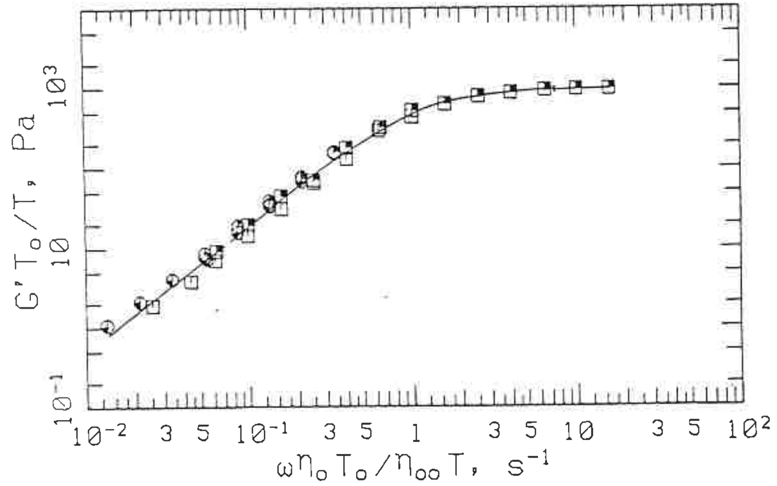


Figure 6. Dependence of reduced storage modulus on reduced frequency for liquor of 75% solids at various temperatures: the squares are for 50°C, η_o=1100 Pa-s; and the circles are for 80°C, η_o=10 pa-s. The reference temperature is 50°C.

The shapes of the dynamic viscosity and storage modulus curves are similar to those of uncrosslinked polymers (Ferry, 1980). This indicates the absence of crosslinking in the liquor tested, even at solids content as high as 75%. Moreover, the success of combining the curves of several temperatures into a single composite curve suggests that the liquor tested can be treated as an uncrosslinked polymeric fluid of low molecular weight.

However, general statements on linear viscoelastic properties of black liquors can not yet be made at this point. The temperature and frequency ranges have to be expanded, possibly to cover a frequency range of ten decades, and liquors of various sources and pulping conditions need to be tested.

6. Conclusions

In the small-amplitude oscillatory shear flow experiments, the black liquors studied, having solids contents up to 75%, behave like uncrosslinked polymeric fluids of low molecuar weight. Composite plots of dynamic viscosity and storage modulus were constructed by using reduced coordinates. The data were taken at temperatures ranging from 40 to 80°C over three decades of frequency.

Notation

h	Gap height in parallel-disk geometry
G'	Storage Modulus
G''	Loss Modulus
r	Radial direction in spherical or cylindrical coordinates
R	Disk radius
t	Time
T	Temperature
$\mathcal{T}$	Torque
z	Axial direction in cylindrical coordinates
η_o	Zero-shear-rate viscosity
η'	Dynamic viscosity
η''	$= G'/\omega$

θ	Angular displacement in parallel-disk geometry, or angle measured downward from vertical axis in spherical coordinates
ϑ_o	Cone angle
μ	Newtonian viscosity
ρ	Fluid density
ϕ	Angular displacement in cone-and-plate geometry
φ	Phase shift
ω	Frequency of oscillation
Superscript o	Amplitude of the variable
Subscript o	Quantity at reference temperature

Literature Cited

Bird, R.B., R.C. Armstrong, and O. Hassager, Dynamics of Polymeric Liquids: Vol. 1 Fluid Mechanics, Wiley, New York (1977).

Co, A., H.K. Kim, M.O. Wight, and A.L. Fricke, "Viscosity of Black Liquors at High Temperatures", Tappi, 65 (8), 000 (1982).

Ferry, J.D., Viscoelastic Properties of Polymers, 3rd ed., Wiley, New York (1980).

Kemeny, T.E. and J.D. Chazin, "Determination of Black Liquor Solids", Tappi, 56 (8), 81-83 (1973).

McDonald, K.L., "Rapid Determination of Kraft Black Liquor Solids", Tappi, 62 (1), 80-81 (1979).

Wight, M.O., "Black Liqour Characterization by Cone-and-Plate and Parallel-Disk Rheometry", M.S. Thesis, University of Maine, Orono, Maine (1982).

Wight, M.O., A. Co and A.L. Fricke, "Viscosity of Black Liquor by Cone-and-Plate and Parallel-Disk Viscometry", AIChE Symposium Series, No. 207, Vol. 77, 1-12 (1981).

B4 - 1

THE EFFECT OF COOKING VARIABLES AND WOOD RAW MATERIAL ON THE PROPERTIES OF BLACK LIQUOR

Eero Korpio
Nils-Erik Virkola

Helsinki University of Technology
Forest Products Department
Laboratory of Pulping Technology
SF-02150 Espoo 15, Finland

Abstract

The aim of this investigation was to examine the changes in the properties of black liquor possibly caused by cooking variables and by wood raw material. The investigation was mainly based on laboratory cooks. The applicability of the results to mill conditions was checked by analysing some mill black liquors. The following properties of black liquor were analysed: carbon, hydrogen, sulphur, sodium and potassium contents of dry solids, soap content, and heat value of dry solids, kinematic viscosity, boiling point rise, density and surface tension. The analytical methods used were found to give well repeatable results.

In cooking pine chips, separate investigations were carried out to find to which extent sulphidity, active alkali dosage, degree of delignification, storing of chips and growth site (southern and northern Finland) of trees influence the properties of black liquor. The effect of using mill white liquor instead of synthetic white liquor was also studied.

The results of spruce and birch cooks and those of cooks containing forest chips (consisting mainly of pine or birch), sawdust and

sawmill chips and unbarked wood chips were compared with the results obtained from pine cooks.

Mill scale results were available on pine and birch cooks and on pine and birch cooks containing forest chips (8-10 %), on pine cooks containing sawmill chips and of softwood sawdust cooks.

The results of the investigation correspond rather well with the dependences reported in the literature. Similarly, the mill trial results supported those obtained in laboratory cooks. Within the scope of this investigation only slight and expected changes in the properties of black liquor were observed.

1. Introduction

The influence of wood raw material and cooking variables on the properties of black liquor has not been investigated systematically. The information collected from the literature is not complete, because all the factors influencing properties of the black liquor have not been mentioned or analysed /1/. The analytical methods used in separate investigations may differ, so the results therefore are not always comparable /1/. To shed more light on the problems in this field, an investigation was carried out in cooperation between the Helsinki University of Technology and the Finnish Recovery Boiler Committee. The investigation was intended to provide comparable information for Finnish conditions about the influence of wood raw material (pine; fresh, stored, growing location, barked, unbarked; spruce and birch, forest chips etc.) and cooking variables (sulphidity, alkali dosage, degree of delignification, synthetic and mill white liquor) on the properties of black liquor. The investigation was mainly based on laboratory cooks, but some comparable mill trials were also carried out /2/.

The main results are given in the following.

2. Cooking of pine chips (from southern Finland)

2.1 Effect of white liquor sulphidity

The effect of white liquor sulphidity was investigated in an experimental series, in which the alkali dosage (22 % as NaOH) and the kappa number (35) were kept constant and the sulphidity was varied (25, 30 and 40 %).

According to Fig. 1, the total pulping yield seems, as expected, to increase with an increase in sulphidity. In Fig. 2 the sulphur and hydrogen contents in the dry solids of black liquor have been plotted against the sulphidity. The sulphur content increases linearily with an increase in sulphidity, while the hydrogen and sodium contents remain nearly constant. The carbon content of the dry solids decreases with an increase in sulphidity (Fig. 3). This is due to the increased pulping yield and the decrease in the amount of dissolved organic matter in the black liquor when the sulphidity increases. The viscosity measured from a black liquor with a temperature of 90 °C and a dry solids content of 55 %, seems to increase slightly with an increase in sulphidity (Fig. 4). Fig. 4 also shows one point referring to the result of a laboratory cook made with a mill white liquor. It is necessary to point out here that the viscosity determination should be made as soon as possible after the cooking. Otherwise disturbances caused by polymerization in the black liquor will take place.

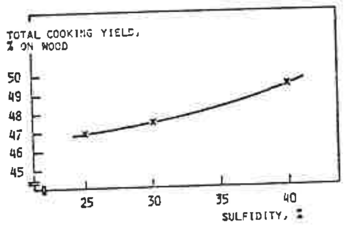


Fig. 1. Total cooking yield of pine kraft pulp as a function of white liquor sulphidity.

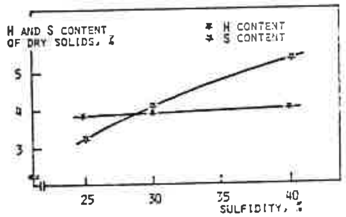


Fig. 2. Hydrogen and sulphur content of pine black liquor dry solids as a function of white liquor sulphidity.

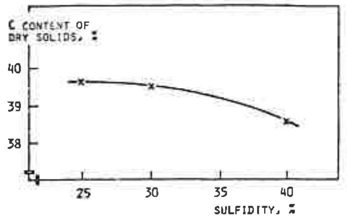


Fig. 3. Carbon content of pine black liquor dry solids as a function of white liquor sulphidity.

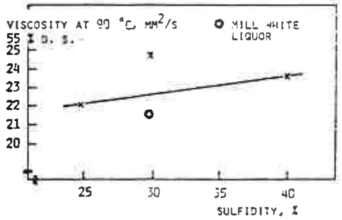


Fig. 4. Viscosity of pine black liquor as a function of white liquor sulphidity, 55 % d.s., temperature 90°C.

Variations in the sulphidity do not cause changes in the boiling point rise of black liquor (dry solids content 30 and 55 %) (Fig. 5). The calorimetric and effective heat values of the black liquor dry solids, as a function of the sulphidity, is shown in Fig. 6. On the basis of the increase in pulping yield and of the decrease in the carbon content in the black liquor dry solids, it can be concluded that the heat value should decrease with an increase in sulphidity.

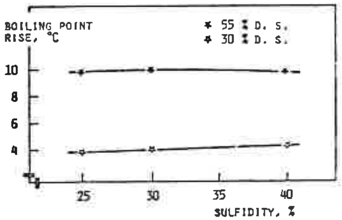


Fig. 5. Boiling point rise of pine black liquor as a function of white liquor sulphidity.

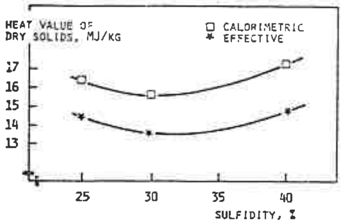


Fig. 6. Calorimetric and effective heat value of pine black liquor dry solids as a function of white liquor sulphidity.

The experimental results show, however, that the cook with the highest sulphidity gives the highest calorimetric heat value. The same applies to the effective heat value. The result is caused

by errors in the calculations; i.e. in the case for the cook of highest sulphidity the sulphur correction used in calculating the effective heat value does not correspond to the reactions occurring in the calorimetric bomb.

It should be noted here that the surface tension of weak black liquor increases only slightly with an increase in sulphidity.

2.2 Effect of the degree of delignification (kappa number)

The effect of the degree of delignification on the properties of black liquor was investigated by cooking the same pine chips with the same white liquor (22 % alkali dosage as NaOH, sulphidity 30 %) to different kappa numbers (25, 35, 45) varying the cooking time at the maximum temperature.

The total pulping yield as a function of kappa number can be seen in Fig. 7. In Fig. 8 the carbon content of the black liquor dry solids has been plotted against the kappa number. According to the figures the carbon content decreases with an increase in the kappa number and the pulping yield.

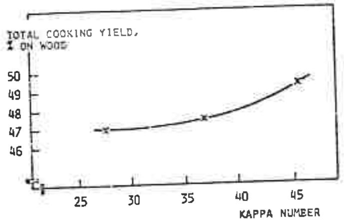


Fig. 7. Total cooking yield of pine kraft pulp as a function of kappa number (22 % NaOH, 30 % sulphidity).

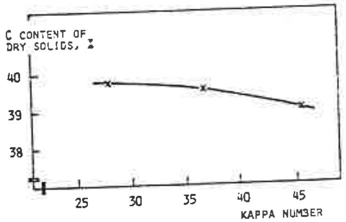


Fig. 8. Carbon content of pine black liquor dry solids as a function of kappa number.

Very small changes were found in the hydrogen and sulphur contents of black liquor dry solids at different kappa number. The hydrogen content decreases and the sulphur content increases slightly with an increase in the kappa number, whereas the sodium content increases clearly (Fig. 9).

The viscosity of the black liquor seemed to increase when cooking to a higher kappa number, but this could not be verified.

The calorimetric and effective heat value of the black liquor decreases clearly with an increase in the yield and a decrease in the carbon content (Fig. 10). The changes in the surface tension values of black liquor were rather small. There is a trend towards slightly higher surface tension when the delignification is continued (Fig. 11).

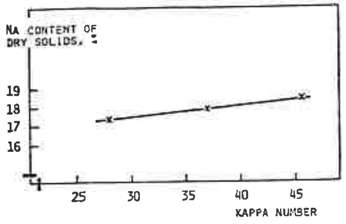


Fig. 9. Sodium content of pine black liquor dry solids as a function of kappa number.

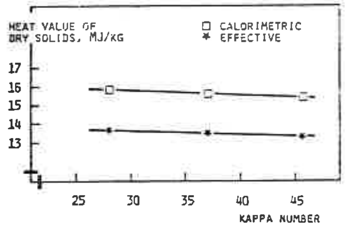


Fig. 10. Calorimetric and effective heat value of pine black liquor dry solids as a function of kappa number.

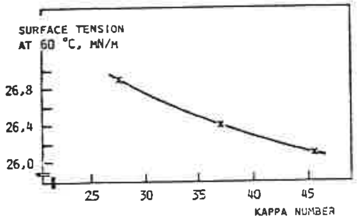


Fig. 11. Surface tension of weak black liquor as a function of kappa number.

2.3 Effect of active alkali dosage

The effect of the active alkali dosage was studied using active alkali dosages of 20, 22 and 24 % as NaOH on b.d. wood. The sulphidity of the white liquor was kept constant (30 %) and the kappa number target was 35. According to Fig. 12 a change in the alkali dosage did not influence the pulping yield. The sulphur content of the black liquor dry solids increases linearily with an increase in the alkali dosage (Fig. 13), but the hydrogen content remains constant.

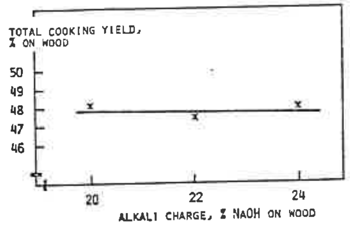


Fig. 12. Total cooking yield of pine kraft pulp as a function of alkali charge.

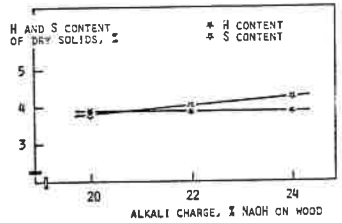


Fig. 13. Hydrogen and sulphur content of pine black liquor dry solids as a function of alkali charge.

The carbon content decreases with an increase in the proportion of inorganic material (Fig. 14).

The viscosity of black liquor with a dry solids content of 55 % decreases markedly with an increase in the alkali dosage (Fig. 15). Fig. 15 also shows one point referring to a cook with a mill white liquor.

The boiling point rise as a function of active alkali dosage for black liquors evaporated to 30 and 55 % dry solids contents are shown in Fig. 16. The boiling point rise increases linearily with an increase in the alkali dose and more clearly for black liquors containing 55 % dry solids. A slight decrease can be found in the calorimetric and effective heat value of black liquor dry solids when using higher

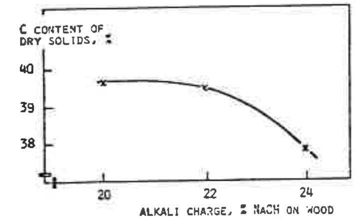


Fig. 14. Carbon content of pine black liquor dry solids as a function of alkali charge.

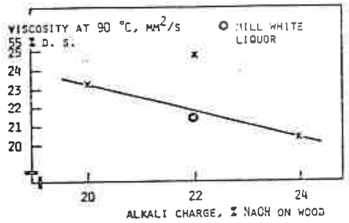


Fig. 15. Viscosity of pine black liquor as a function of alkali charge, 55 % d.s., temperature 90^{o}C.

amounts of active alkali (Fig. 17). This is in good agreement with the above mentioned decrease in the carbon content. The surface tension of weak black liquors decreases rather clearly with an increase in the alkali dosage (Fig. 18).

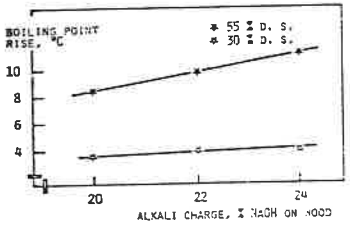


Fig. 16. Boiling point rise of pine black liquor as a function of alkali charge.

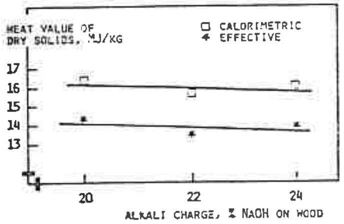


Fig. 17. Calorimetric and effective heat value of pine black liquor dry solids as a function of alkali charge.

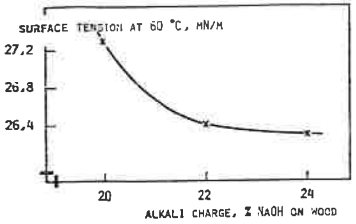


Fig. 18. Surface tension of weak black liquor as a function of alkali charge.

2.4 Effect of chip drying and storage

This part of the investigation was carried out so that the same pine chip portion was cooked fresh, dried and stored in a moist condition for 5 months at a temperature of 4 ^{o}C in plastic bags, after which it was dried. Each sample was cooked with the same active alkali dose and with a white liquor having sulphidity of 30 %. The main results are shown in Table 1.

It can be established that drying of chips is decreasing the total pulping yield somewhat in spite of the decrease in the extractives content. Storage of chips causes an apparent increase in the pulping yield. When cooking fresh chips, the carbon and hydrogen contents are slightly lower than when cooking dried chips. On the contrary when cooking stored and thereafter dried chips, especially the carbon and sulphur contents are clearly lower, but also the hydrogen content is slightly lower.

The heat values can be explained by differences in pulping yield for fresh and dried chips. The higher heat values of stored chips cannot be explained by pulping yield or carbon content of the black liquor.

Drying and storage of chips produce an increase in the viscosity and the surface tension of black liquor. The soap content naturally decreases during drying and storage of chips. Storage of chips causes a clear increase in the boiling point rise.

2.5 Effect of the growth site of pine

This part of the study was carried out by cooking pine mill chips from southern and northern Finland. The study included also a mill trial (Veitsiluoto Oy) with pine chips. The main results are listed in Table 2. Pine from northern Finland gives a clearly lower pulping yield, which partly can be explained by the higher extractives content. Black liquor dry solids of pine from northern Finland has a higher carbon content than the corrsponding black liquors of pine

Table 1. Properties of black liquors originating from cooks of fresh, dried and stored and thereafter dried pine mill chips

Chip sample	Kappa number	Pulping yield	Black liquor properties								
			Dry solids					Viscosity mm²/s 55 % D.S. 90°C	Soap content of dry solids, %	Boiling point rise °C 55 % D.S.	Surface tension mN/m
			C	H	S	Heat value, MJ/kg					
		%	%	%	%	calori-metric	effective				
Fresh	33.4	48.3	39.08	3.80	4.10	15.2	13.1	21.5	3.5	11.0	25.6
Dried	36.9	47.5	39.54	3.93	4.10	15.7	13.6	24.8	2.6	9.9	26.4
Stored and dried	34.9	49.3	37.19	3.60	3.39	16.0	14.1	25.4	1.0	12.2	28.2

Table 2. Properties of black liquors originating from cooks made with pine chips from southern and northern Finland

Chip quality	White liquor	Kappa number	Pulping yield	Black liquor properties							
				Dry solids						Soap content	Viscosity mm²/s 55 % D.S. 90°C
				C	H	S	K	Heat value, MJ/kg			
			%	%	%	%	%	calori-metric	effective	%	
Southern Finland	synthetic	36.9	47.5	39.54	3.93	4.10	0.11	15.7	13.6	2.6	24.8
Southern Finland	mill liquor	36.1	47.7	37.58	3.96	4.20	1.54	15.3	13.2	0.75	21.6
Northern Finland	synthetic	36.9	45.0	40.47	4.15	4.03	0.08	16.4	14.2	3.6	25.2
Northern Southern Finland	mill trial	34.3	-	39.74	3.86	4.07	1.38	16.2	14.1	1.7	28.1

from southern Finland, when comparing the black liquors produced by synthetic or mill white liquors. Mill white liquor laboratory and mill cooks gave black liquor dry solids with less carbon than the corresponding synthetic laboratory cooks. Mill white liquors contain more inorganic inert material; for example the potassium content is much higher.

Heat values black liquors from cooks with northern Finnish pine are about 5 % higher than those of corresponding black liquors of southern Finnish pine. This can be explained by the difference in the pulping yield and also by the higher soap content in the black liquor.
The viscosity values (55 % D.S., 90 $^{\circ}C$) indicate that pine from northern Finland causes higher values. It was also found that there is no difference in the boiling point rise between black liquors from cooks with northern and southern pine.

3. Effect of adding spruce wood

In Finland kraft pulp mills commonly use mixed softwoods, i.e. pine and spruce. To investigate the effect of spruce wood an experimental series was made cooking a mixture of pine and spruce (1:1), and pure spruce and pine separately. 22 % active alkali as NaOH on b.d. wood and white liquor with a sulphidity of 30 % were used to achieve a kappa number of 35.

The results obtained show that the pulping yield increases when more spruce wood is used (Fig. 19). 100 % spruce wood gives a pulping yield about 1.5 percentage points higher than corresponding 100 % pine wood (from southern Finland). The carbon content of the black liquor dry solids decreases with an increase in the proportion of spruce (Fig. 20). Changes in the hydrogen and sulphur contents were very small.

Heat values decrease slightly with an increase in the proportion of spruce wood (Fig. 21). There is a trend towards lower black liquor viscosity (55 % D.S. content and 90 $^{\circ}C$) when spruce wood is mixed with pine. There is still some uncertainty about the viscosity value originating from the 100 % pine cook using mill white liquor (Fig. 22).

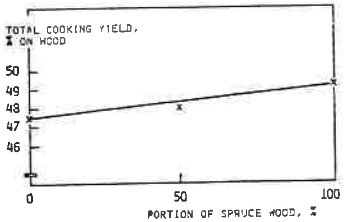


Fig. 19. Total cooking yield of pulp as a function of spruce wood portion.

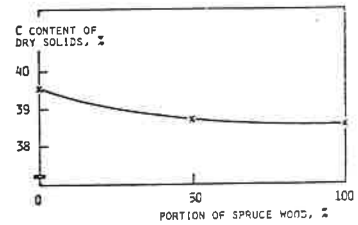


Fig. 20. Carbon content of black liquor dry solids as a function of spruce wood portion.

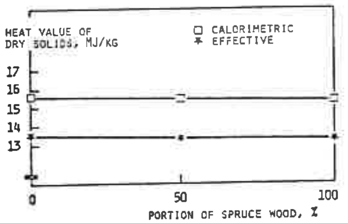


Fig. 21. Calorimetric and effective heat value of black liquor dry solids as a function of spruce wood portion.

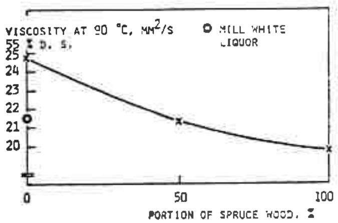


Fig. 22. Viscosity of black liquor as a function of spruce wood portion, 55 % d.s., temperature 90^{o}C.

4. Summarized results of miscellaneous experiments

4.1 Addition of forest chips consisting mainly of pine

These experiments were carried out so that 20 % of forest chips consisting mainly pine were mixed with normal pine bole wood chips from southern Finland. This mixture caused a slight increase in the carbon content and the heat value of the black liquor dry solids. Corresponding increase were found in viscosity, boiling point rise and surface tension. When in a mill scale experiment about 10 % forest chips consisting mainly of pine was mixed with normal bole wood chips from northern Finland, the results were almost opposite to those in the above-mentioned laboratory experiment. The differences in the properties were rather small.

4.2 Addition of sawdust and sawmill chips

Adding 10 % of sawdust to the wood (pine from southern Finland) raw material in laboratory experiments did not change the carbon content, but reduced the sulphur and sodium contents of the black liquor dry solids. When cooking sawdust only in a mill scale experiment, the carbon and hydrogen contents of the black liquor dry solids were low because of the very high alkali dosage, which is necessary in mill scale sawdust cooking.

Because the yield is lower in cooking sawdust than in cooking bole wood chips, adding 10 % sawdust to the chips causes higher black liquor heat values. Black liquors from 100 % sawdust cooking in mill scale have low heat value because of the high content of inorganic matter. Because of the high alkali dosage in mill scale sawdust cooking, the viscosity values of black liquor are clearly lower.

Mixing sawmill chips with bole wood pine chips (from southern Finland) (1:1) causes higher carbon and hydrogen contents in the black liquor dry solids. Black liquor heat values are also clearly higher. In a mill scale trial 60 % of pine bole wood chips (from northern Finland) was mixed with 40 % of sawmill chips. The results were compared in a mill trial with 100 % pine bole wood chips (from northern Finland). Adding sawmill chips seems to cause a decrease in the carbon and hydrogen contents of the black liquor solids. The black liquor had about the same heat values, but the viscosity, boiling point rise and surface tension seemed to be somewhat lower when adding sawmill chips.

4.3 Effect of unbarked softwood chips

Unbarked softwood chips (bark content 4.5 %) were cooked in laboratory experiments and the black liquor was analysed. The analysis showed that the carbon content and heat value of the black liquor solids were slightly higher than in corresponding cooks with barked wood. Differences in viscosity and boiling point rise were found to be small. The surface tension was greater for unbarked wood.

4.4 Effect of mixed (pine + birch) filling black liquor

In batch cooking of softwood and birch wood simultaneously, mixed black liquor is used as filling liquor. A cooking experiment was made with pine chips using black liquor containing 50 % pine and 50 % birch black liquor. The results showed that black liquor caused a slight decrease in the carbon and hydrogen content of the black liquor. Correspondingly the viscosity decreased and the boiling point rise and surface tension value increased.

5. Cooking birch wood chips (from northern Finland)

The experiments were carried out using birch wood chips from northern Finland. To achieve a kappa number of about 20 with birch from northern Finland more active alkali has to be used (24 % as NaOH, sulphidity 30 %) than when cooking birch wood from southern part of Finland.

Because of the higher pulping yield and high content of inorganic chemicals in the black liquor, the calorimetric and effective heat values are clearly lower for birch black liquor dry solids than for pine kraft black liquor. Black liquor evaporated to 55 % dry solids showed a high boiling point rise (13.2 ^{o}C), i.e. several degrees higher than the corresponding softwood black liquors (Table 3). The viscosity of black liquors produced in these laboratory cooks at 55 % dry solids in 90 ^{o}C was only half of the viscosity of softwood black liquor. The surface tension of weak birch black liquor was 1.8 - 3.7 mN/m higher than for softwood black liquors.

Widely diverging results were obtained when cooking pure birch bole wood chips and these mixed with forest chips (8 %) consisting mainly of birch in mill scale (Veitsiluoto Oy), as can be seen from some results listed in Table 3.

Table 3. Black liquor properties obtained in laboratory and mill scale cooking of birch and birch mixed with forest chips (8 %) consising mainly of birch

Scale	Chips	Sulphidity %	Active alkali % NaOH	Kappa number	Black liquor properties				
					C % in D.S.	H % in D.S.	Calorimetric heat value MJ/kg D.S.	Viscosity mm²/s 55 % D.S. 90°C	Boiling point rise 55 % D.S. °C
Laboratory	birch bole	30	24	19.4	35.47	3.37	14.3	10.5	13.2
Mill	"	37.4	27	18.9	34.95	3.60	15.3	763(*	12.0
Mill	birch forest chips	37	26.8	18.1	36.10	3.88	15.7	415(*	11.0

*) Black liquor samples from flash tank contained granules and the viscosity could not be determined. Viscosities were measured from samples of the intermediate black liquors.

The sulphur and potassium contents of the mill black liquor were much higher than in the laboratory cooks because of higher white liquor sulphidity and closed water circulation. The black liquor carbon content was slightly higher in laboratory cooking than in corresponding mill cooking. Forest chips increase the carbon and hydrogen contents. In mill scale trial, black liquor heat values were higher than in laboratory cooks and are not much lower than in corresponding softwood cooks. Cooking of forest chips mixed with birch wood shows the highest value. This is well in agreement with the higher carbon content in black liquor dry solids. The high soap content increases the heat values, because the intermediate black liquor has about 0.4 - 0.8 MJ/kg D.S. lower calorimetric heat values. On the other hand, the lower extractives content of birch chips used in laboratory cooks leads to lower black liquor heat values.

The viscosity values of the intermediate black liquor are very high as can be established from the figures given in Table 3. Black liquor samples taken from flash tanks (continuous digester) contained granules so the viscosity values could not be determined. The surface tension values of mill black liquors were as high as those of the black liquor from laboratory cooks. In mill scale experiments the boiling point rises were 1 - 2 °C lower than in laboratory cooks.

6. Reliability of the results

The reliability of the analysis used in the investigation was tested. According to these tests very good repeatability was found in the following analyses:

- sodium and potassium contet
- carbon content
- calorimetric heat value
- density of 30 % D.S. black liquor
- boiling point rise
- surface tension

The repeatability was also found to be fairly good in other analyses. Therefore, the results can be regarded very reliable.

7. Notes about some analytical methods

When determining the boiling point rise of 30 % and 55 % D.S. black liquors overheating took place, which weakened the reliability of the determination.

In the determination of the black liquor soap content the representativeness of the sample taken was not necessarily the best.

As already mentioned above, storage of black liquors for viscosity determinations might have caused changes in the viscosity values.

8. Conclusions

Some general conclusions based on the results of the investigation can be drawn:

The carbon and hydrogen contents of black liquor dry solids correlate very well with the total pulping yield; the carbon and hydrogen contents decrease with an increase in the pulping yield. The sulphidity of the white liquor has clearly the greatest effect on the sulphur content of the black liquor. The sodium content seems to depend, except on the alkali dosage, also on the pulping yield. The potassium content in mill scale black liquors was 10 to 20 times that in corresponding laboratory cooks.

The calorimetric heat value of black liquors depends very strongly on the carbon content. The relationship between heat value and carbon content found in the literature corresponds very well with the findings of this investigation.

According to the literature the viscosity of black liquors depends, when the dry solids content and temperature are constant, on the ratio between inorganic and organic substances. When this ratio decreases, the viscosity of black liquors increases. Such a trend could also be found in this study, although this ratio was not determined. The viscosity values correspond with the values found in this investigation.

The boiling point rise of black liquors depends, according to the literature, when the black liquor solids content is constant, also on the ratio between inorganic and organic substances. When the proportion of inorganic substances increases, the boiling point rise increases, too. Similar conclusions could be drawn during this investigation.

The results of black liquor density determinations are in good agreement with the information given in the literature. The density increases as a function of the black liquor dry solids content and of the proportion of inorganic substances. The influence of wood species on the density could not be explained.

The surface tension values found in this study showed that the surface tension value increased with an increase in the ratio between inorganic and organic substances in the black liquor. The degree of this influence is not clear. The values found were lower than reported in the literature.

In general the results obtained correspond rather well with the dependences described in literature. Mill trials supported the results obtained in laboratory cooks. Within the scope of this investigation only slight changes in the properties of black liquor could be observed.

9. Experimental

9.1 Laboratory experiments

The following wood raw materials were used:

- pine chips (Pinus silvestris) from southern and northern Finland
- spruce chips (Picea abies) from southern Finland
- birch chips (Betula verrucosa) from northern Finland
- sawdust and sawmill chips from northern Finland
- whole-tree chips from southern and northern Finland
- undebarked chips

The chips were air-dried and screened with a modified William screen and the fraction of 2-6 mm thickness was accepted for pulping.

The chips were pulped in a forced-circulation 20-litre laboratory digester. The white liquor was prepared using SCAN-N 2:63 standard method. The cooks were performed under the following conditions: total alkali 20 - 24 % as NaOH; sulphidity 25-40 %; liquor-to-wood ratio 4; time to max. temperature (80-170°C) 90 min; and time at 170°C 90-230 min. In laboratory experiments (22) in each experimental point three parallel cooks were made, one to get black liquor filling liquor for two parallel cooks.

9.2 Mill experiments

Mill trials were carried out in a Kamyr continuous vapour-liquid phase digester equipped with a preimpregnation tower in the mill of Veitsiluoto Oy. The following combinations of wood raw material were used:

- 100 % pine chips
- 90 % pine chips and 10 % forest chips consisting mainly of pine
- 60 % pine chips and 40 % sawmill chips
- 100 % birch chips
- 92 % birch chips and 8 % forest chips consisting mainly of birch

The total active alkali charge was 23 - 27 % NaOH and the sulphidity 35 - 37 %.

The sawdust cooks were performed in the Tervasaari mill of United Paper Mills Ltd with a sawdust digester (Bauer M & D) equipped with a post cooking zone. The average temperature is 182°C and cooking time 20 min to reach a kappa number of 20.

9.3 Analyses

The kappa number of the pulps was determined using SCAN-C 1:77 standard method.

The following standard methods or methods of the Finnish Pulp and Paper Research Institute were used for analysing the black liquor properties:

sulphur content	FPPRI 63:64
carbon and hydrogen content	FPPRI 62:64
dry solids content	SCAN-N 22:77
boiling point rise	ASTM D 1120
heat value	FPPRI 66:81
viscosity	ASTM D 445

The sodium and potassium contents of the black liquors were determined with a flame photometer. The soap content was determined using a method introduced by Saltsman and Kuiken /3/. The surface tension was determined with a stalagnometer at 60 $^{\circ}$C /4/. The density was determined with a pyknometer at two different dry solids contents, the temperature being 20°C.

Acknowledgement

The authors would like thank J. Heiko, M.Sc. (Eng.) (Veitsiluoto Oy), A. Jaakkola, M.Sc. (Eng.) (Ekono Oy), V. Mikkola, M.Sc. (Eng.) (Oulu Oy) and L. Söderhjelm, M.Sc. (Eng.) (FPPRI) for the valuable discussions and help during the study.

References

1. "Properties of Spent Liquors in Chemical Pulping Industry, Part I: Literature Study; Part II: Analyses of Mill Spent Liquors". Study made by EKONO for the Energy Division of the Ministry of Trade and Industry in Finland (in Finnish), 1981.

2. Korpio, Eero: "The effect of cooking variables and wood raw material on the black liquor properties", M.Sc. (Eng.) Thesis work, Helsinki University of Technology, Laboratory of Pulping Technology (in Finnish), 1982.

3. Saltsman, W., Kuiken, K.A.: Estimation of tall oil in sulphate black liquor. Tappi 42(1959)11, 873-874.
4. Linkoaho, M.: Fysiikan työt 1. Otakustantamo, 4. painos, Espoo 1978. 154 pages (in Finnish).

LATEST DEVELOPMENTS IN BLACK LIQUOR EVAPORATION

by

A. Ahonen, Manager, Section Pulp and Paper
B. Jungerstam, Senior Specialist, Process and Energy
Y. Nygårdas, Manager, Process Engineering Department
EKONO Consulting Engineers, Helsinki, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

LATEST DEVELOPMENTS IN BLACK LIQUOR EVAPORATION

A. Ahonen
B. Jungerstam
Y. Nygårdas

EKONO Consulting Engineers, Helsinki, Finland

1. General

In this paper we will first describe how the general conditions in the pulp mill have changed and are changing, including

- energy costs
- fuel/power price relationships
- energy/equipment cost relationships
- degree of closing the mill water circulation, and
- increasing demands for pollution control.

These changes affect, of course, the selection of evaporation plant equipment, when one is aiming at an optimum design for the whole mill. How the changed mill conditions and the present situation should be taken into account will be analyzed below in more detail.

The following items will be discussed:

- present optimum number of stages in the evaporation plant
- vapor recompression (VRC) versus multiple effect evaporation
- influence of environmental aspects on the technology (e.g. integration of stripping the dirty condensates from an energy point of view)
- balancing of changes in the energy structure in the mill by means of correct evaporation plant selection (e.g. pre-evaporation alternatives)
- increase of the dry solid content in the heavy black liquor.

Possible solutions to the above questions will be described in more detail by means of some cases. The economic impact of the changed mill conditions will be shown by case calculations.

2. Changes of mill conditions

Figure 1 shows the increase of fuel and power prices as well as the equipment cost increase during the last ten years in Finland. The marginal price of fuel (heavy oil) has increased about tenfold during this period whereas the equipment costs have increased about three and a half times. The relative price of coal has also increased by the same order of magnitude as for oil. It is evident that the optimum conditions for evaporation have changed in the direction of lower fuel consumption and higher investments.

The price of power has increased about fivefold during the same period. The relatively slower increase of electric power price (in comparison to fuel) affects the optimum equipment selection, e.g. the feasibility of VRC evaporation will increase compared to multiple effect evaporation.

The pulp mills have to increase the closure of their water circulation because of stricter environmental requirements on one hand and the increased energy prices on the other. Today, with modern technology it is possible to reach a total water consumption of below 50 m^3 per ton of pulp whereas ten years ago the water consumption of Finnish pulp mills was generally in the order of 200-300 m^3 per ton of pulp.

When a pulp mill has decreased its water consumption the demand of secondary heat (warm and hot water) will consequently decrease. This means e.g. that the feasibility of the VRC evaporation will increase when compared to multiple effect evaporation where warm water (40...50°C) is produced "free of cost" and hot water (70...80°C) can be produced at a low price. In a VRC-plant the production of warm and hot water is usually negligible.

The feasibility of pre-evaporation plants which use blow steam or flash steam from the digester will increase further as the demand of hot water in the process decreases. However, hot water can also be produced in blow or flash pre-evaporation if the dimensioning of the plant is correct.

The tightened pollution control requirements will necessitate increased treatment of dirty condensates. For this reason it is obvious that the integration of the stripping process is very important from an energy point of view. In this paper some examples will be given of how to connect condensate stripping to multiple effect evaporation or VRC evaporation.

The choice of the evaporation plant is also influenced by the primary energy balance as well as the extent of energy self-sufficiency desired at the mill.

Figure 2 shows the energy balance of a modern bleached kraft pulp mill which can be achieved using modern technology. If all available bark is burned and if oil is used as fuel in the lime kiln, the steam balance shows a surplus of about 2 GJ/ADT.

Because the possibilities to deliver steam to outside consumers from a market pulp mill are normally limited, the optimum evaporation plant configuration is no longer a six-stage plant; the optimum number of stages is lower to match the "excess" steam.

The situation is however different if bark and other normally available waste fuels are used in the lime kiln (e.g. by gasification of bark). In this case excess steam is almost completely eliminated by choosing a six-stage evaporation plant.

The situation is different if the mill is not a market pulp mill but part of an integrate with other consumers of steam and electricity (e.g. an integrated pulp/fine paper mill).

3. Number of stages in the evaporation plant

Figure 3 shows the optimization of the number of stages in the black liquor evaporation plant for some fuel and power prices of today.

It can be seen that beyond stage six the effective temperature difference of each stage will decrease rather quickly because of the boiling point rises and because the k-values of the rising film units no longer remain constant. For these reasons the required heating surface will increase considerably.

In sulphite mills where the boiling point rises are negligible a seven-stage evaporation is today often the optimum plant configuration.

Selecting the evaporation plant and optimizing the number of stages is very important for the energy balance of the whole mill. The pulp mill steam and power balance as well as the mill secondary heat balance can be adjusted by the correct choice of the evaporation plant, even after equipment selection has already been done in the other process departments.

4. VRC (vapor recompression) evaporation

In comparing VRC and multiple effect evaporation costs, the relatively high power/steam price ratio on the one hand and the valuable secondary heat (warm/hot water) production on the other in most cases used to favor the choice of multiple effect evaporation.

As the power/steam price ratio has decreased, and the secondary heat demand of the pulp mill has decreased as well because of closing the water circulation system, VRC evaporation is becoming an interesting alternative today.

Figure 4 compares a six-stage multiple effect evaporation plant and VRC evaporation. In this graph the benefits of warm/hot water production have not been accounted for.

5. The influence of environmental aspects

To meet the environmental requirements with a system which makes good economic sense puts strong demands on the dirty condensate stripping system. For this reason much development work has been done e.g. to integrate the stripping process with a VRC evaporation plant. Figure 5 shows an interesting example of how to carry out the stripping of methanol in connection with a VRC evaporation plant producing 65% heavy black liquor. In this case the heavy liquor unit is parallel with two units in series producing intermediate black liquor. The stripping column is coupled in series with the stage evaporating intermediate black liquor.

There are several ways to integrate stripping with a multiple stage evaporation plant. The optimum configuration depends among others on the amount of condensate which has to be stripped and which it pays to strip. Figures 6 and 7 show how some suppliers have solved the integration of stripping with multiple effect evaporation.

6. Pre-evaporation with secondary heat from the cooking plant

Figures 8 and 9 show some examples of how, in principle, the secondary heat from the cooking plant can be used in the pre-evaporation of weak black liquor.

Figure 8 shows a blow heat evaporation plant built at the New Zealand Forest Products kraft pulp mill. The blow heat from the batch cooking plant is recovered in a conventional hot water accumulator. The accumulator water and steam serve as a heat source for a three-stage falling film pre-evaporation plant.

Figure 9 shows some basic solutions for the two-stage recovery of black liquor flash heat from a continuous digester by using either a multiple effect evaporation plant or a Lockman column.

7. Increasing the DS-content of black liquor

The common interest of evaporation plant suppliers today seems to be rather strongly directed towards the means and equipment for raising the final DS-content of black liquor without an unreasonably high cost increase of the concentrators.

Figure 10 shows, using a rough calculation, the economic importance of the DS-increase. This calculation has been carried out for an increase of the DS-content from 62% to 67% using conventional forced circulation concentrators.

It is evident that using a falling film type concentrator where the power consumption is considerably lower, the payback period can be even shorter. Today some manufacturers of forced circulation concentrators also seem to direct their development efforts towards solutions with less power consumption than today's conventional forced circulation units.

8. Summary

This paper has attempted to illustrate the importance of selecting the correct evaporation system for today's kraft pulp mill.

The development work carried out in this field demonstrates that the means exist to balance and optimize the mill primary and secondary energy systems, even after selecting the process technology in the other mill departments, by correctly choosing the evaporation plant.

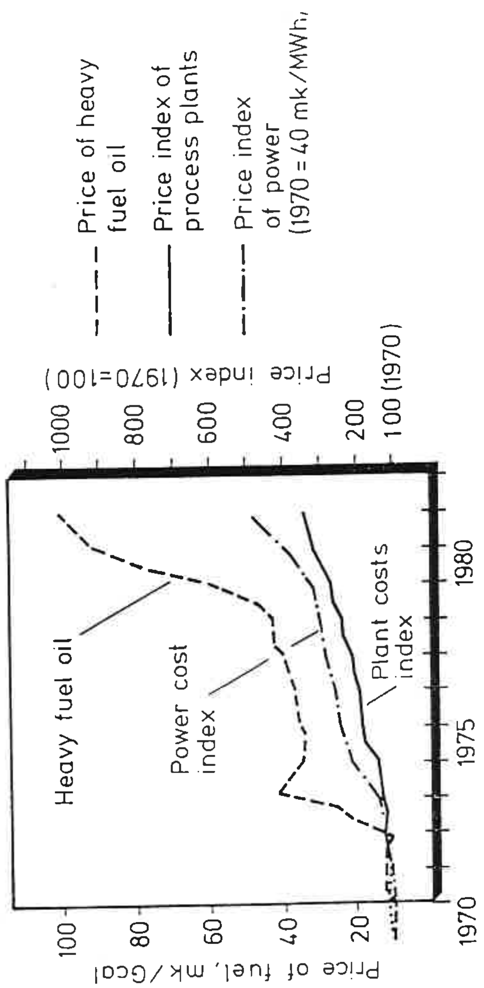


FIG. 1
DEVELOPMENT OF ENERGY PRICES AND EQUIPMENT COST INDEX

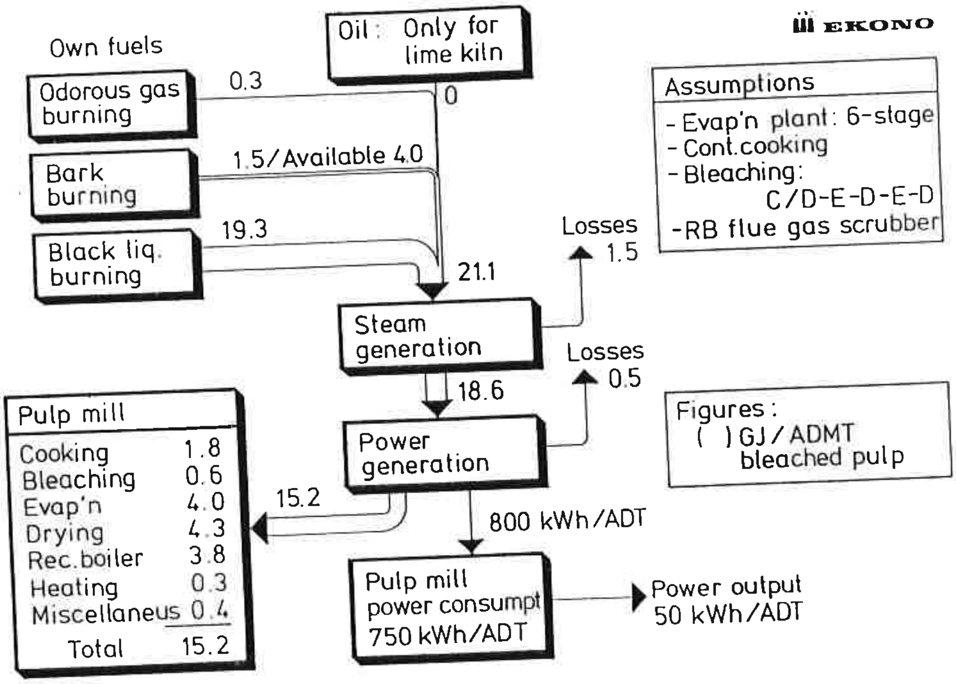
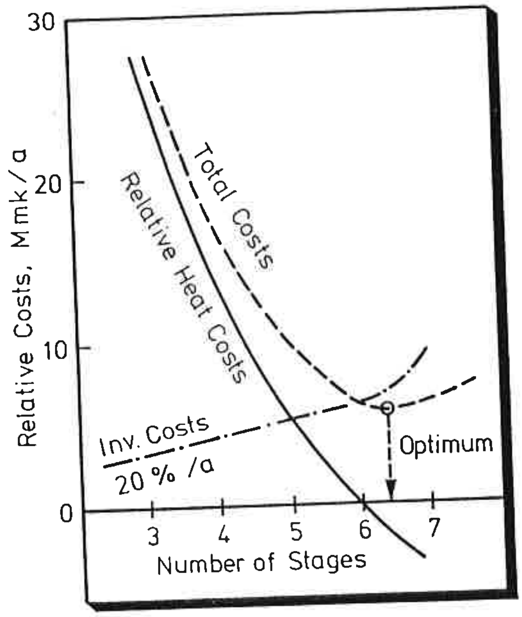


FIG. 2
KRAFT PULP MILL HEAT BALANCE, ANNUAL AVERAGE



Capacity: $360\ tH_2O/h$

Evaporation rate: $300\ tH_2O/h$ (Average)

Costs: -Back pressure steam: 23 mk/GJ
-Power: 180 mk/MWh

DS-Content of Heavy Black Liquor: 65 %

FIG. 3

OPTIMIZATION OF NUMBER OF STAGES ON A BLACK LIQUOR EVAPORATION PLANT

EKONO

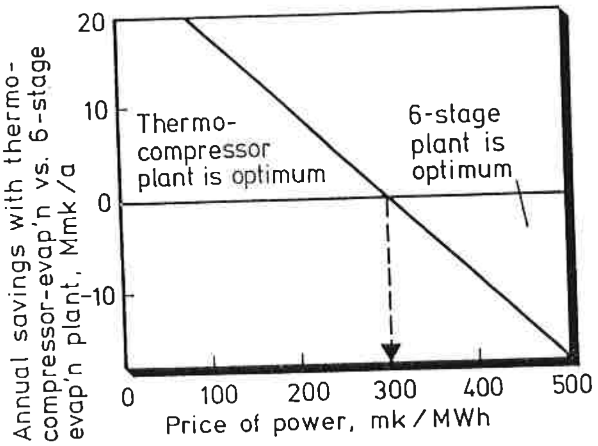


FIG. 4 COMPARISON OF THERMOCOMPRESSOR AND A 6-STAGE BLACK LIQUOR EVAP'N PLANT

Assumptions:

- Heat consumption of 6-stage plant: 480 MJ/t H_2O
- Power consumption of the compressor: 36 kWh/tH_2O (ΔT_{eff} = 8 °C)
- Heavy black liquor D.S.-content: 65 %
- Evap'n rate (Average): 300 t H_2O/h
- Annual operation time: 8 300 h/a
- Steam cost: 23 mk/GJ
- Value of secondary heat = 0

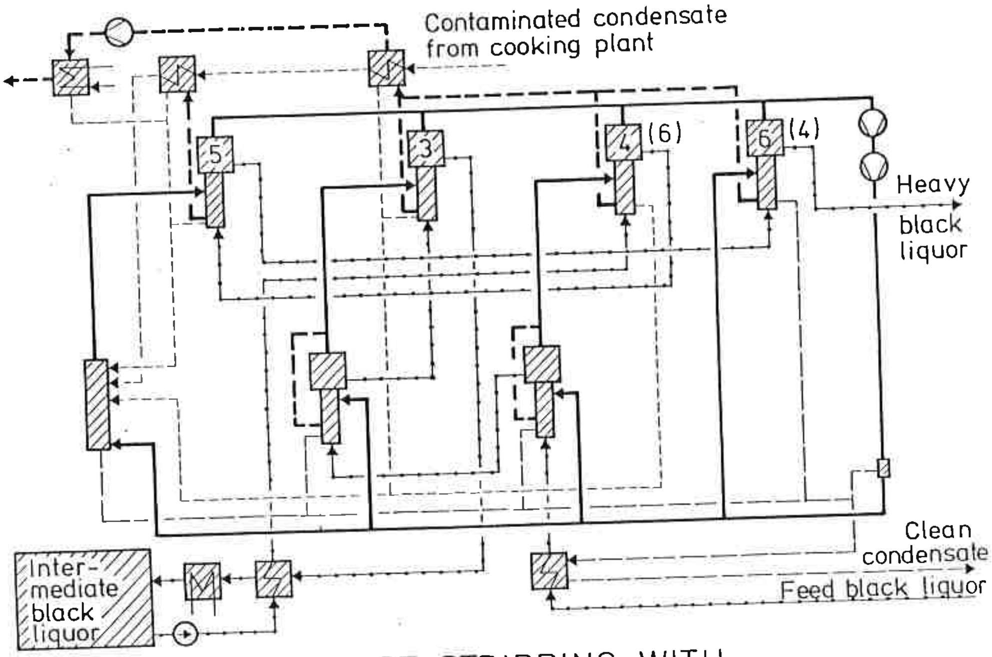


FIG. 5 INTEGRATION OF STRIPPING WITH A VRC EVAPORATION PLANT

EKONO

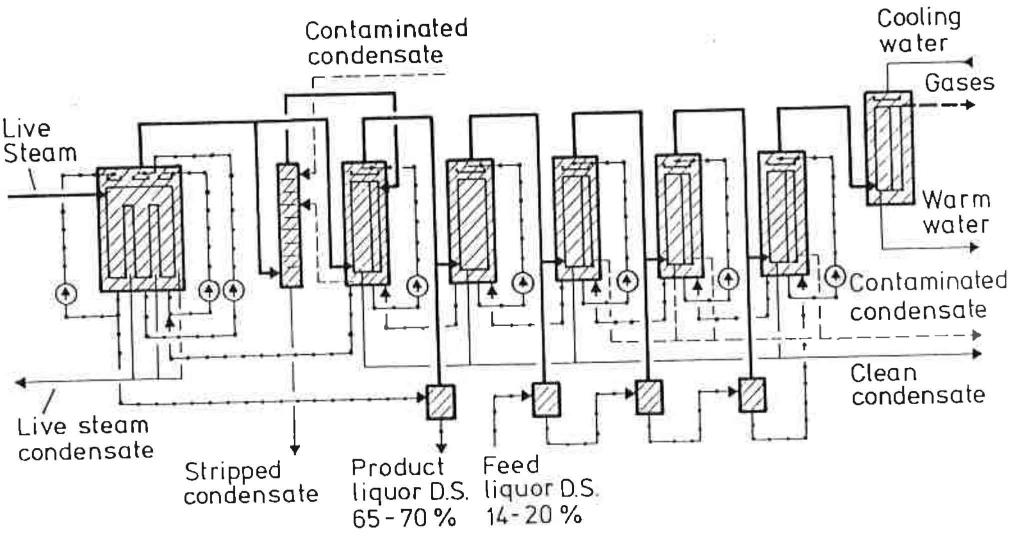


FIG. 6 INTEGRATION OF STRIPPING TO A MULTIPLE EFFECT EVAPORATION EXAMPLE 1

EKONO

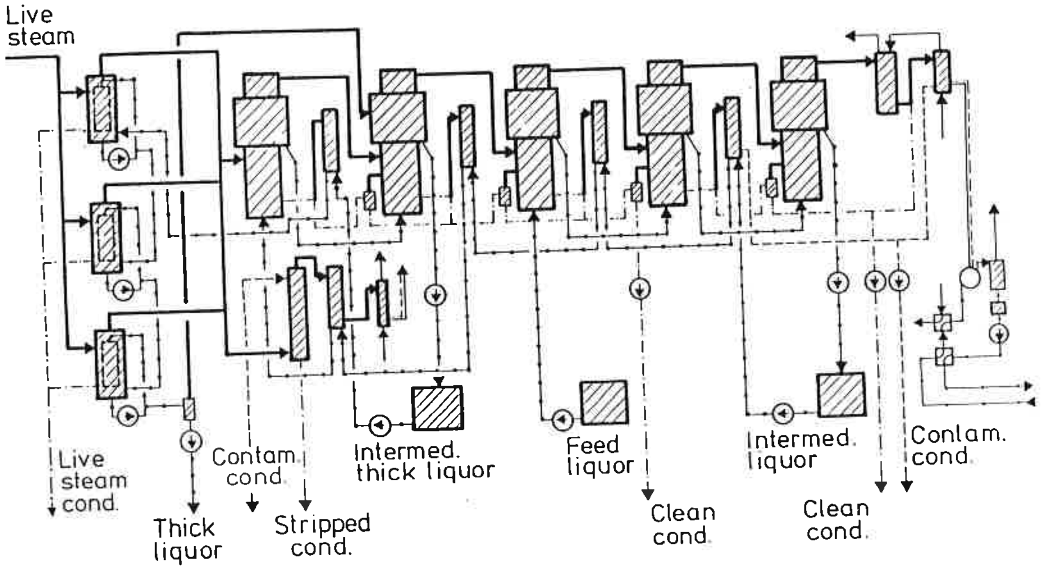


FIG. 7 INTEGRATION OF STRIPPING TO A MULTIPLE EFFECT EVAPORATION EXAMPLE 2

EKONO

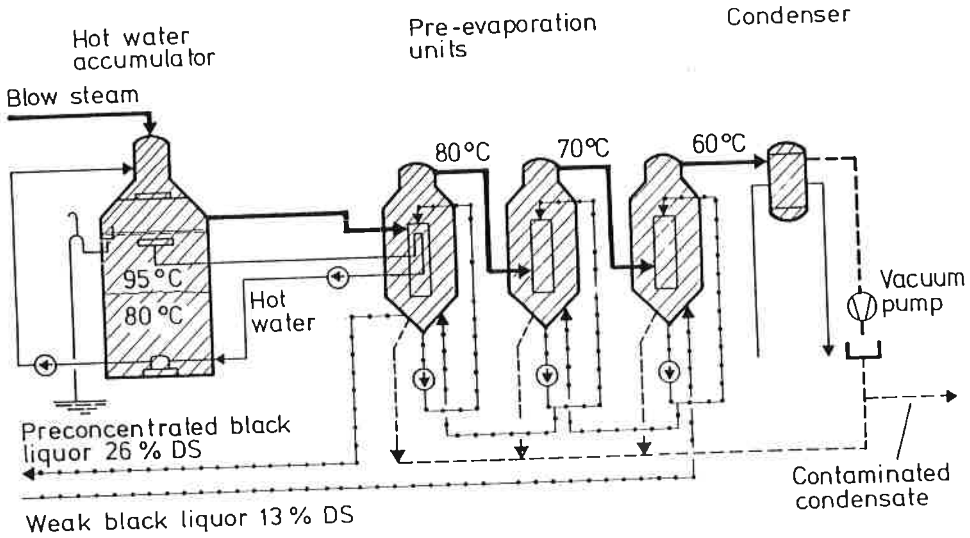


FIG. 8 BLACK LIQUOR PRE-EVAPORATION IN A BATCH COOKING PLANT

EKONO

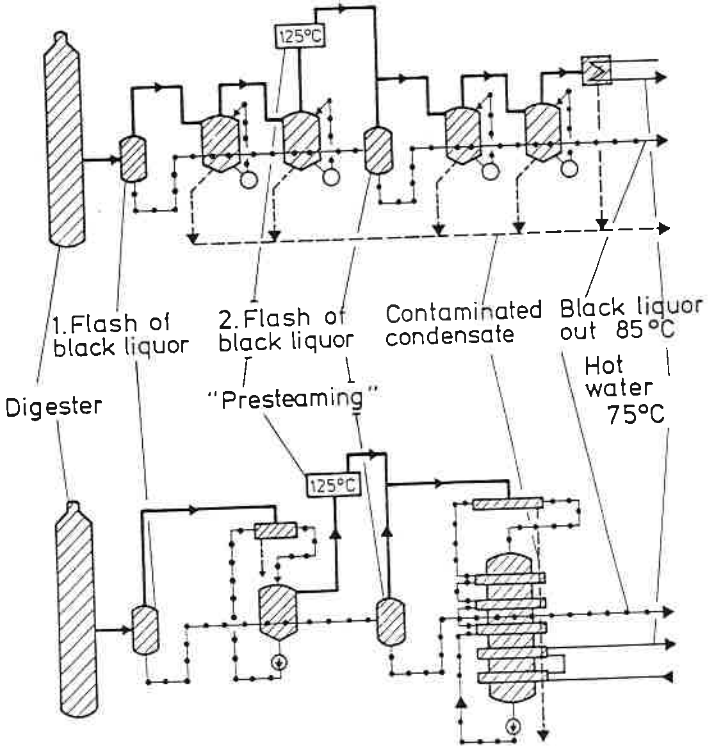


FIG. 9
BLACK LIQUOR PRE-EVAPORATION IN A CONTINUOS COOKING PLANT

Explanation	Unit	Value	Cost Mmk/a
Evaporated water amount (example)	tH_2O/h	300	
Heavy liquor amount	tDS/h	75	
– " – with 62 % DS-content	t/h	121	
– " – " 67 % DS- "	t/h	112	
difference	tH_2O/h	9	
Total saving in fuel oil with 67 % DS black liquor	Gcal/h	4,23	+ 3,7
Additional power consumption in the evaporation plant	kW	450	
Improvement in back pressure power generation	kW	270	
difference	kW	180	- 0,3
Savings in operation costs			+ 3,4
Investment			- 5,4
"Return of Investment" ROI	% / a	63%	
Pay-back-Periode	a	1,6	

FIG: 10

ECONOMICAL ASPECTS WHEN INCREASING BLACK LIQUOR DRY SOLID CONTENT FROM 62 TO 67 %

EKONO

SOME NEW DEVELOPMENTS IN THE RECOVERY CYCLE

by

G. Wiklander, Senior Consultant, Process Technology
Industrins Processkonsult AB - IPK, Sweden

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

SOME NEW DEVELOPMENTS IN THE RECOVERY CYCLE

G Wiklander, Senior Consultant, Process Technology,

INDUSTRINS PROCESSKONSULT AB - IPK, Sweden

Some time ago I happened to come across a short paper in TAPPI for February 1977. I had read the paper in 1977 and then forgotten about it and now I did find that a short sentence could serve as a motto for my process philosophy. The paper was written by Mr J F Paul Eschner, St. Regis Paper Co and the sentence I refer to reads as follows:

"IN MOST ANY PROCESS, TAKING A GOOD LOOK AT WHAT GOES IN WILL HELP ONE TO EVALUATE WHAT'S GOING TO COME OUT."

This is, in my opinion, an extremely good advice which is followed too seldom. Very often things are taken for granted, instead of discussing what really is happening in the process.

Many of the process industries, not the least the pulp and paper industry, are plagued by a rather common misconception, which can and very often does cause production disturbances and extra operating costs. This misconception is that if you install enough process controllers, or to be modern, enough computer control all over the plant, all disturbances in the process will disappear and you can live happily ever after.

It is quite clear that automatic control, in one form or another, is a good thing and absolutely necessary for today's large and complicated process industries. But in some processes you may have parameters that simply cannot be controlled, because some part of the process works in an unpredictable way, making control difficult or even impossible.

Experiences have shown that some of the larger recovery boilers, pulp production over say 600-700 metric tons per day, can have large uncontrollable variations in a very important process parameter, namely the smelt flow. It is not possible to measure the smelt flow directly, but fairly accurate flow data can be arrived at indirectly.

In 1976 we got the first reliable information concerning the smelt flow variations from a large boiler. The plant had a very good instrumentation system with measured data recorded through a computer. Because of this the recorded values of the different variables were synchronized in time. (Fig. 1)

Fig. 1 shows data for some parameters in the dissolving tank. The dashed curve shows the in-flow of weak liquor to the tank. It is at once clear that large flow variations are occurring. The unbroken line shows the measured density of the green liquor in the tank. The density has varied from 1 180 to about 1 230 kg/m^3.

From the data given in Fig. 1 it is quite easy to calculate the outflow of the green liquor, taking into account the variations in the liquor level in the smelt tank. Shortly after 8 a.m. the liquor level went down from 79 to 75 % in about 15 minutes. This change in level is equal to a volume of 16 m^3, going out of the tank in 15 minutes. The outflow thus increased with 1 m^3/min or 60 m^3/h over the incoming weak liquor.

The results of the calculations are shown in Fig. 2. The variations in the green liquor flow are very large. At 8 a.m. the flow go up from 50 to more than 300 m^3/h.

To these large variations in the green liquor flow to the clarifier come other disturbances, variations in the green liquor density. If we go back to Fig. 1 we can see that the green liquor density went down from about 1 230 to 1 210 kg/m^3 shortly after 8 a.m. The same phenomena are occurring shortly before 7 a.m. A sharp drop in liquor density is accompanied by an increase in the green liquor flow.

Now, someone may argue that the variations in weak liquor flow, green liquor flow and density are caused by a poor control system. The data we get from Fig. 1 makes it, however, possible to calculate the smelt flow from the furnace. The calculation can be somewhat influenced by a poor control system but the control system cannot change the smelt flow.

The result of the smelt flow calculations are shown in Fig. 3. We can see that the variations in the smelt flow are fairly large. The 3 1/2 hours shown in this figure are not an exception. The diagrams from the mill show about the same variations day after day.

Personally I am quite sur that these smelt flow variations are typical for the mill from which the basic data were taken. The mill has a rather large recovery boiler with a nominal capacity of about 1 800 t/24 h of DS. I am also quite sure that smelt flow variations are common in the larger boilers of the type we have in Sweden. When you have a furnace bottom area of 100 m^2 or more, you have no control of what happens in the turmoil in the furnace. Black liquor ash can form dams, that hinder the smelt to reach the smelt spouts continuously.

Thus, I consider it a proven fact that the green liquor flow from the smelt tank can vary considerably and that the density control has quite a job to keep up with these variations.

A varying flow of green liquor with a varying density is pumped directly to the green liquor clarifier, which works with gravity as the separating principle. I have been unable to collect data on the size and the specific gravity of the particles to be separted in the clarifier. I have, however, experience of a water treatment floatation plant, in which one wall had large glass windows making direct observations possible. Even rather small temperature variations caused large convection currents in the tank, making havoc of the floatation efficiency. A drop in green liquor density from 1 230 to 1 210 kg/m^3 in a short time is equivalent to a temperature rise of about 50°C. Combine this with an increase in flow of 500-600 per cent. If the green liquor is to be handled under these conditions, one should not ask for a clarifier but a miracle.

I am not a chemical engineer and I am not versed in the finer points of the causticizing process. My colleagues tell me, however, that it is rather important for this process, that the green liquor is well clarified before the causticizing starts.

An insufficently clarified green liquor will give problems in the causticizing and make the causticizing degree vary. In this connection I will show a diagram, which my colleague Egon Gustafsson presented at our Recovery Boiler Conference in 1977. Fig. 4.

The figure shows the variations in the active alkali in a white liquor, hour for hour during a normal operating period of 24 hours. The mean value is 129 g/litre but the variations are rather large, up to almost 140 and down to 120. The causticizing is not working properly and some of the problems may depend on a badly clarified green liquor.

What then about getting better clarifying conditions?

The first thing to do is to even out the flow variations. This is easily done by arranging a tank between the smelt tank and the clarifier. By letting the level in this tank vary the outflow to the clarifier can be kept constant. We can use the flow values from Fig. 2 to show how it works out. Fig. 5.

In this case the maximum peak over the mean flow value corresponds to a liquor volume of 85 m^3. That means that a tank volume of $2 \cdot 1.5 \cdot 85 = 250$ m^3 should be enough to even out the flow variations. The factor 1.5 is a safety margin.

To take care of the density variations an extra volume with very good mixing is needed. If we assume perfect mixing, which in practice never is attainable, the dynamics of a mixing tank can be simplified (according to Donald Campbell in Process Dynamics).

Figure 6 shows the simplified conditions. Into a tank with the liquor volume V m^3 Q m^3/h of liquor flows. Some liquor parameter e.g. density has the value γ_i. At the time t_o the density goes up to a peak $(\gamma_i + \Delta\gamma_i)$ and stays there for the time a. Then the density drops back to γ_i.

The tank is assumed to have a perfect mixing equipment. That means that the inflow is mixed at once completely with the content of the tank. The result of this mixing is that the peak $\Delta\gamma_i$ going into the tank is diminished in the outflow. The maximum response in the outflow is $\Delta\gamma_o$. The approximate formula for calculating is very simple. The ratio between the outgoing response $\Delta\gamma_o$ and the ingoing peak $\Delta\gamma_i$ is equal to the duration time of the pulse divided by the hold up time in the vessel.

If we go back to Fig. 1 we can see that the variations in green liquor density are of two kinds, one rather fast with a period of about 10-15 minutes and another one with a period of about one hour. The second kind is connected with the variations in the smelt flow and it could possibly be somewhat reduced by refining the control system.

In this case, if we should arrange a mixing tank volume of around two hours retention time the fast variations would practically disappear and the slow ones would be reduced to one half. Two hours retention time is equal to around 280 m^3 and we had 250 m^3 before to take care of the flow variations. That means that for the mill described a tank with a volume of 550-600 m^3 could serve both as a storage tank and as mixing tank.

In the modernization of a mill in Sweden, in which we have taken part, a green liquor mixing tank has been installed. Before discussing the results from this installation I will show some data from the plant before it was modernized.

Fig. 7 shows the effective alkali content of the white liquor during 1981. The figures given are mean values for every week, in some cases there are half-week means values. The variations are rather large. Behind these means values we have still larger variations on an hourly basis.

Even if the variations of the effective alkali content can be compensated for by varying the liquor charge to the digesters, the variations bring about disturbances in the whole recovery cycle.

When this plant was modernized we put in a combined storage and mixing tank between the dissolving tank and the green liquor clarifier. This new tank had an effective liquor volume of around 550 m^3.

The modernized plant, which was more or less a completely new plant was started up in the middle of May 1982. We thus have not been able to get data for longer running periods yet but the results so far are rather good. Fig. 8 shows the effective alkali content of the white liquor on a day to day basis up to June 21. It must be remembered that the data shown here refer to the daily means of the effective alkali content. There were some disturbances in the plant around May 20-25 and the plant had a scheduled stop May 27 to June 3, 1982.

Fig. 8 also shows the standard deviations for the daily means.

I'll end my lecture by touching some points where new development seems to be needed.

The modern recovery boiler got its real start right after the war. The capacity at that time was more or less standardized to 90-110 tons of pulp per day. Since then the capacity has increased almost continuously and the evolution in Sweden can be seen from Fig. 9. For about 10 years after the war the normal boiler capacity was 100-200 tons per day. Then around 1956 the capacity started to increase and today we have boilers for more than 1 200 tons of pulp per day.

The increased boiler capacity has been followed by certain changes in the process parameters. Our organization has tested practically all of the Swedish recovery boilers. In this manner we have got a rather complete collection of operating parameters for the different mills and the different boiler capacities. We can also follow changes in operating parameters during the years. Some of the changes found may have been caused by the increased dimensions of the recovery boilers. As the changes may influence the operating conditions and the economy, studies in these areas are clearly indicated.

The first observation is that the gross heating value of the dry substance in the liquor seems to go down when the boiler capacity goes up. Fig. 10 gives an overall view. Most of the points in this figure represents the mean of several analyses, in some cases up to 10 different. In practically all mills we have found that when the mill started a new and larger boiler, the heating value went down somewhat.

I have not tried to make statistics out of these data. It is, however, quite clear that statistically the heating values for a new larger boiler belongs to another population than the heating values for an old smaller boiler in the same mill.

We have another parameter, which is connected to the heating value of the dry substance, but where the relations to the boiler capacity are not quite so clear, namely the reduction degree. Fig. 11 shows our data for this case. There are certainly some indications that a larger recovery boiler has a lower reduction degree than a smaller boiler. A couple of the very large boilers are working with a rather low reduction degree.

We have also found a quite clear tendency that the larger boilers are operating with a higher dust load in the flue gases than the smaller boilers. The circulating dust means a further decrease in the heating value of thick liquor sprayed into the furnace.

The decrease in the reduction degree means an increase in dead-load. It can also bring about an increase in the emission of SO_2. Therefore, the combustion conditions of the modern, large recovery boilers should be studied in detail.

Data from the dissolving tank

Fig 1

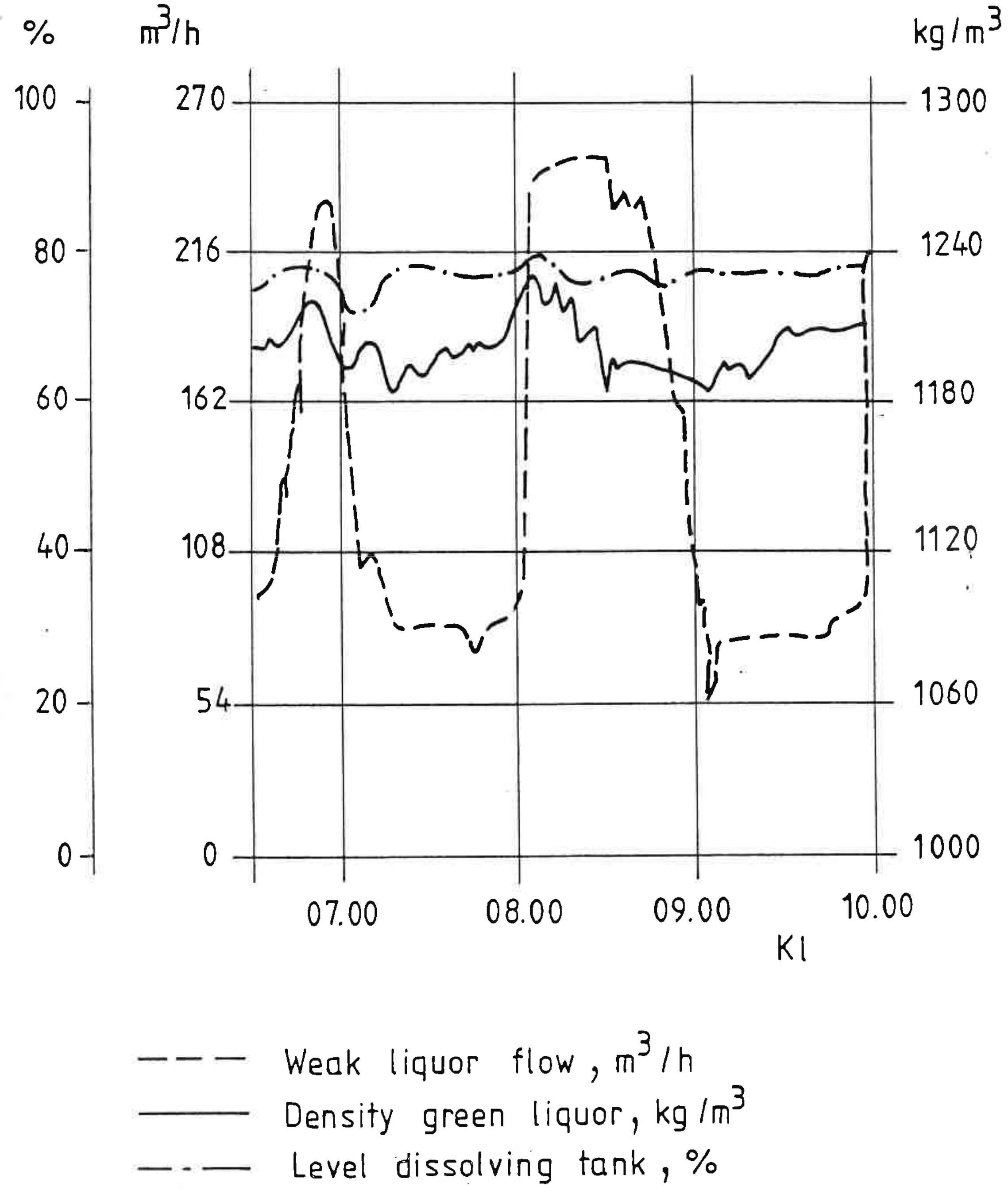
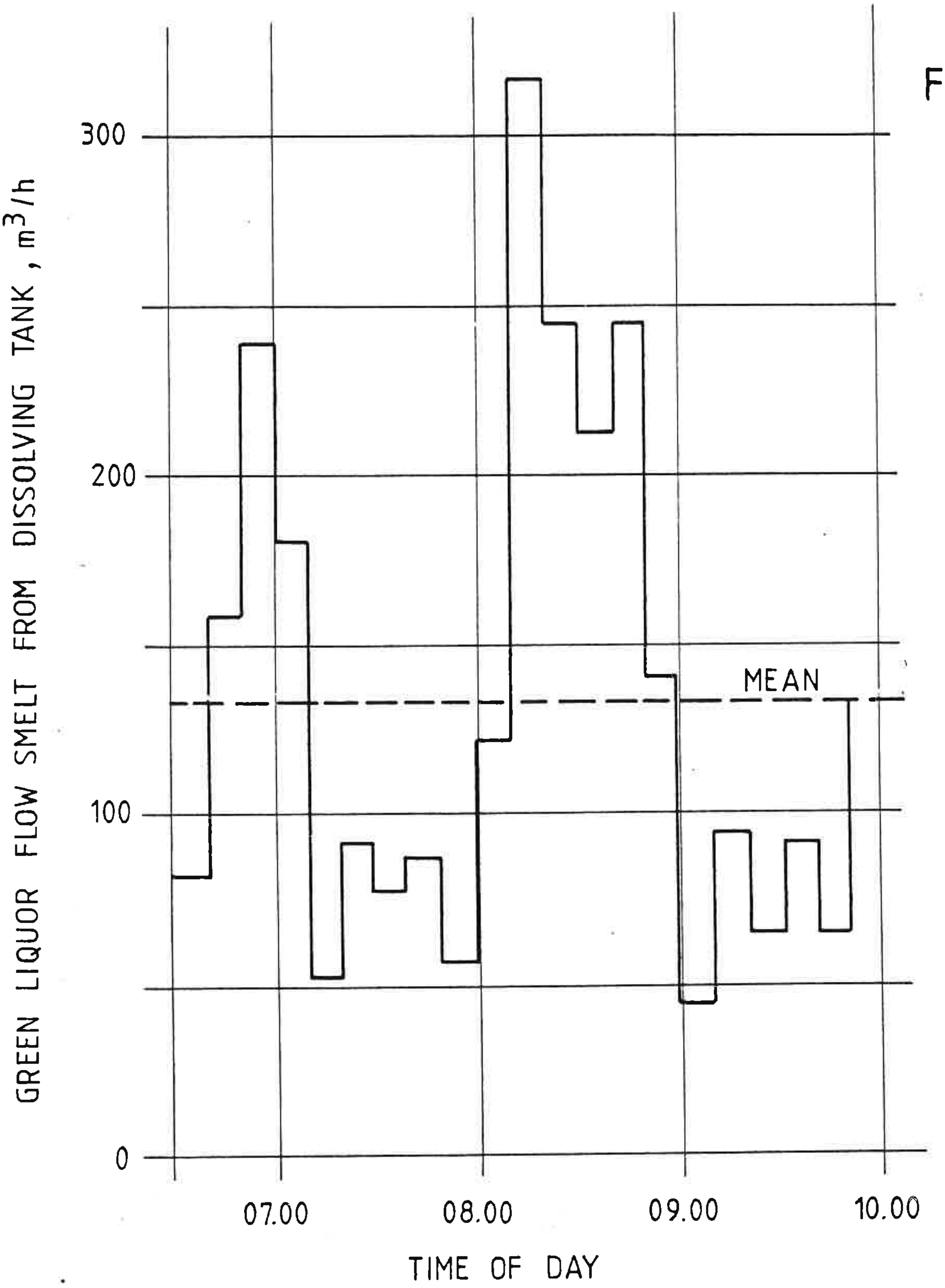


Fig. 2



CALCULATED VALUES OF THE GREEN-LIQUOR
FROM THE SMELT DISSOLVING TANK

CALCULATED VALUES OF THE SMELT FLOW TO THE DISSOLVING TANK

Fig.3

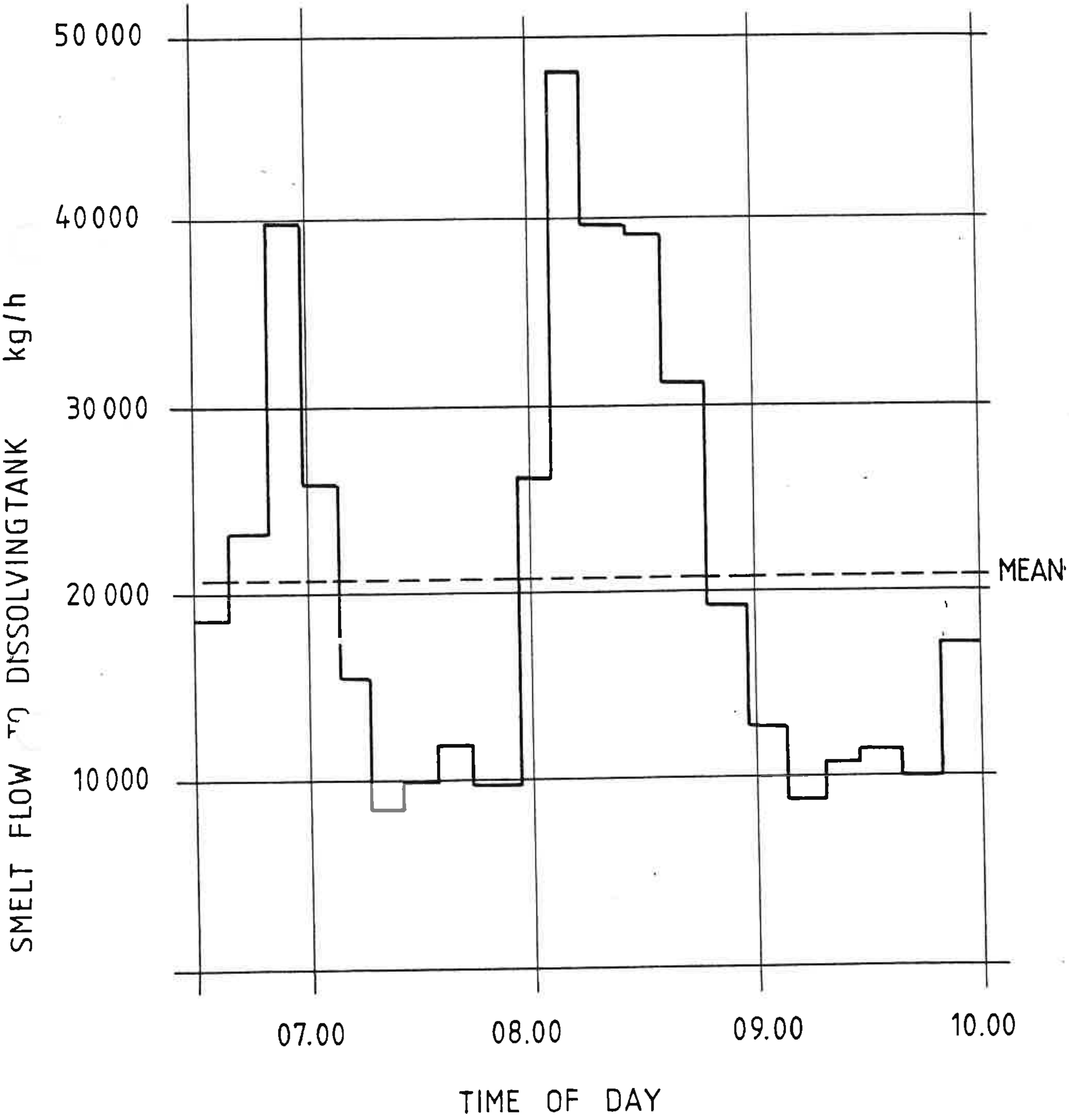


Fig.4

ACTIVE ALKALI IN WHITE LIQUOR IN A MILL.

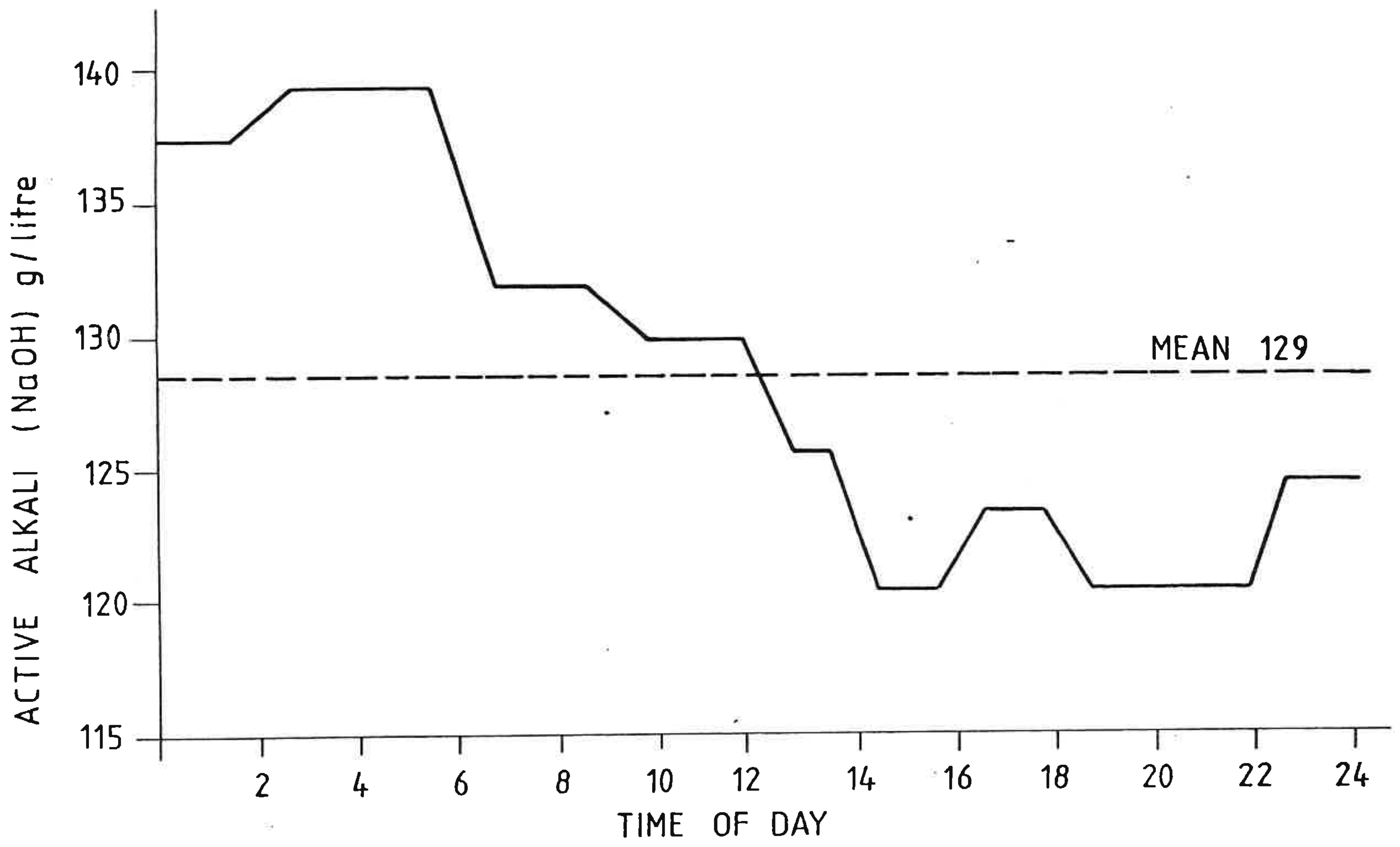
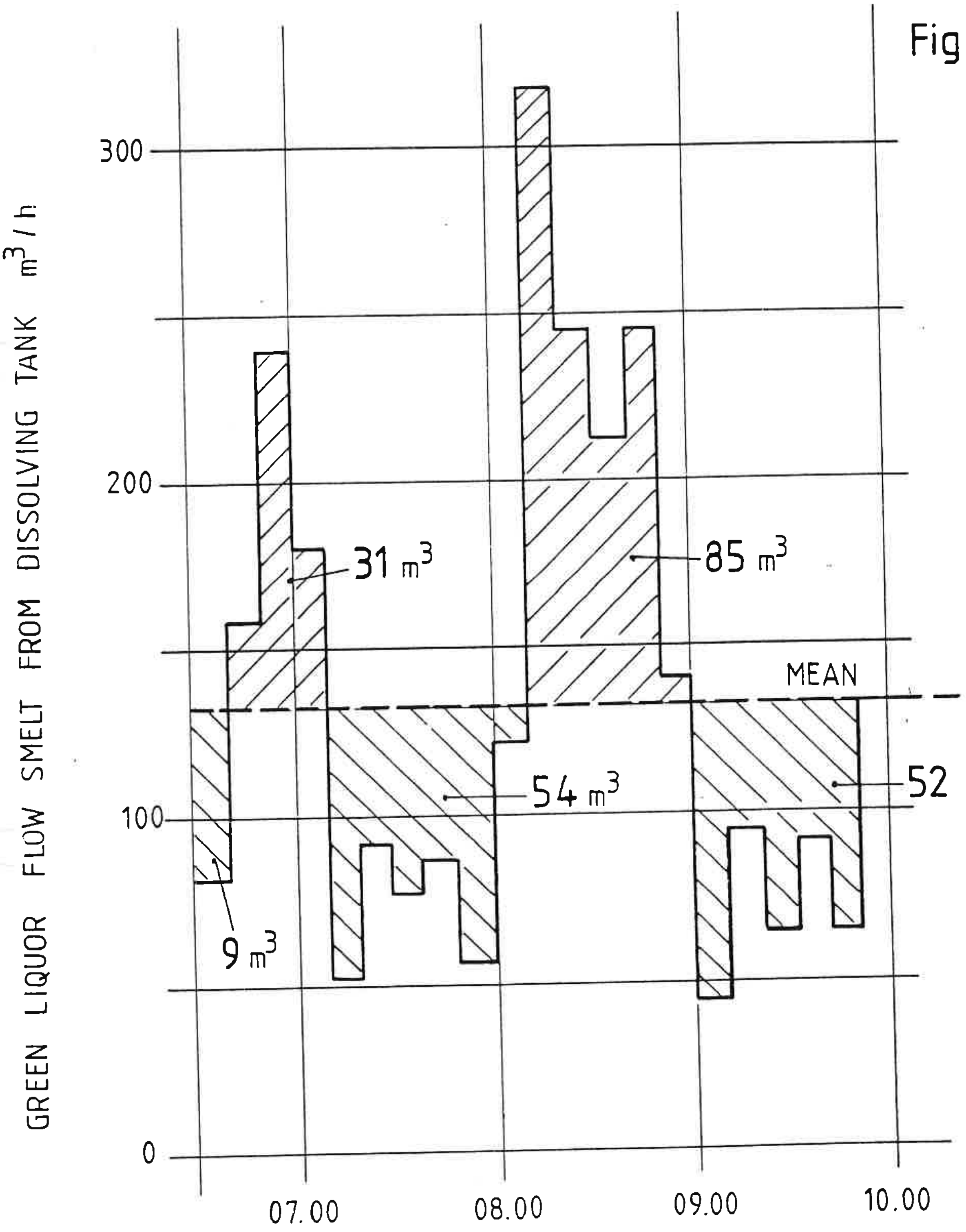
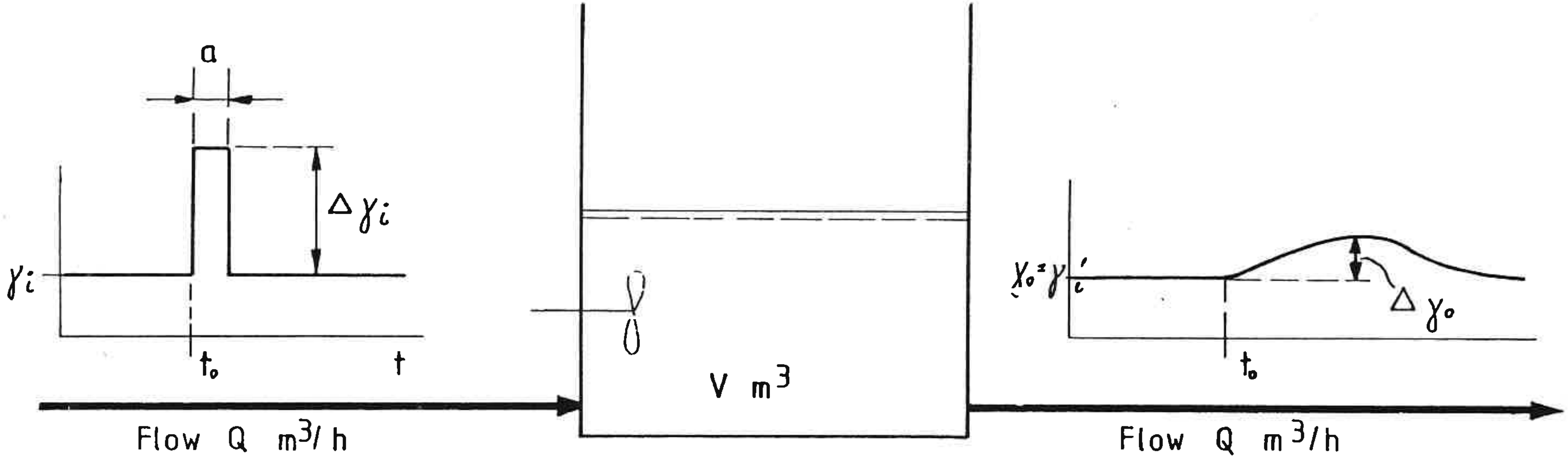


Fig.5



GREEN LIQUOR FLOW VARIATIONS AROUND THE MEAN FLOW VALUE

Fig. 6

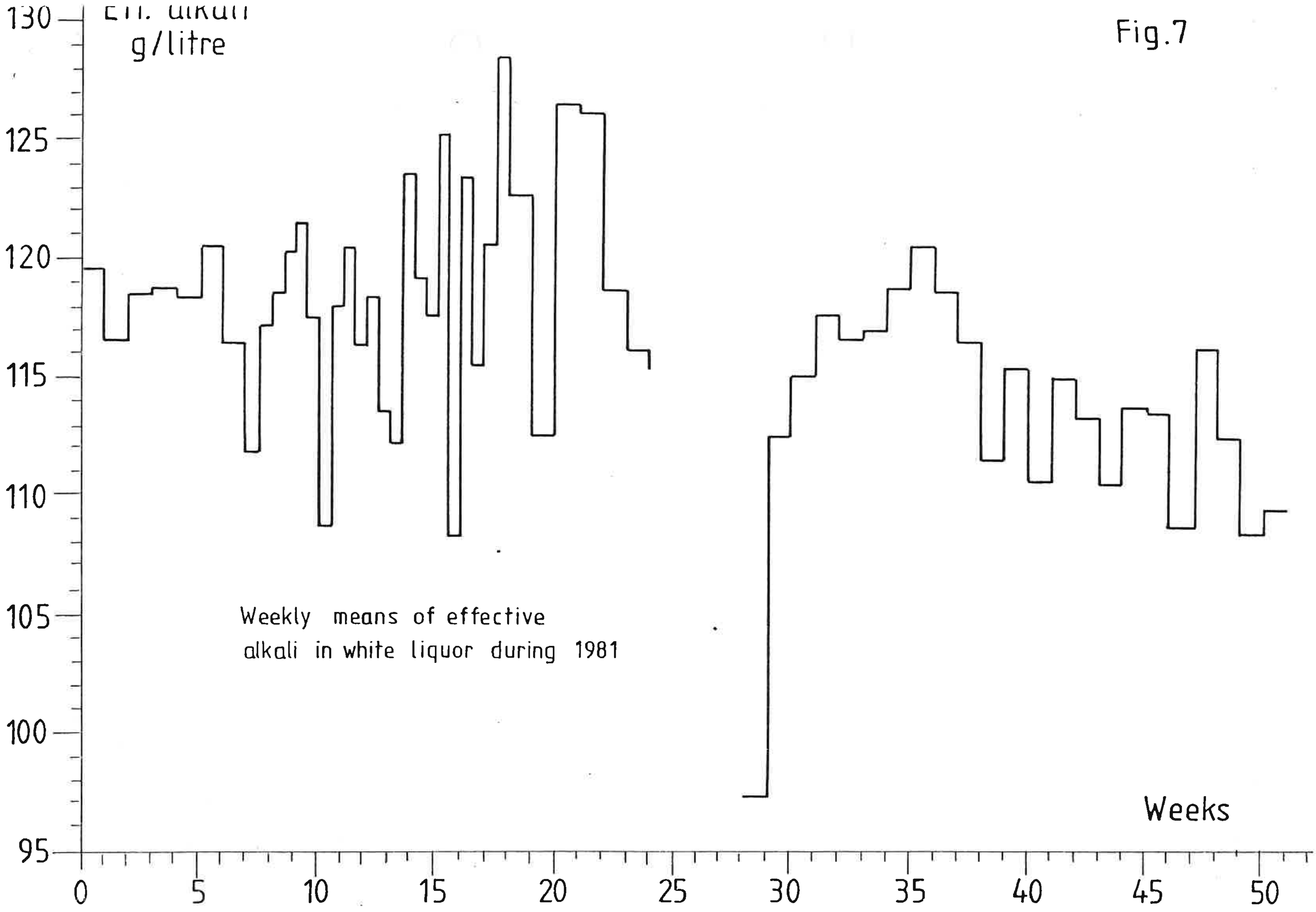


$$\frac{\Delta \gamma_0}{\Delta \gamma_i} \sim a \cdot \frac{Q}{V} \quad ; \quad \frac{V}{Q} = T$$

$$\frac{\Delta \gamma_0}{\Delta \gamma_i} = \frac{a}{T}$$

Pulse response for a perfectly mixed tank

Fig.7



Weekly means of effective alkali in white liquor during 1981

Fig 8

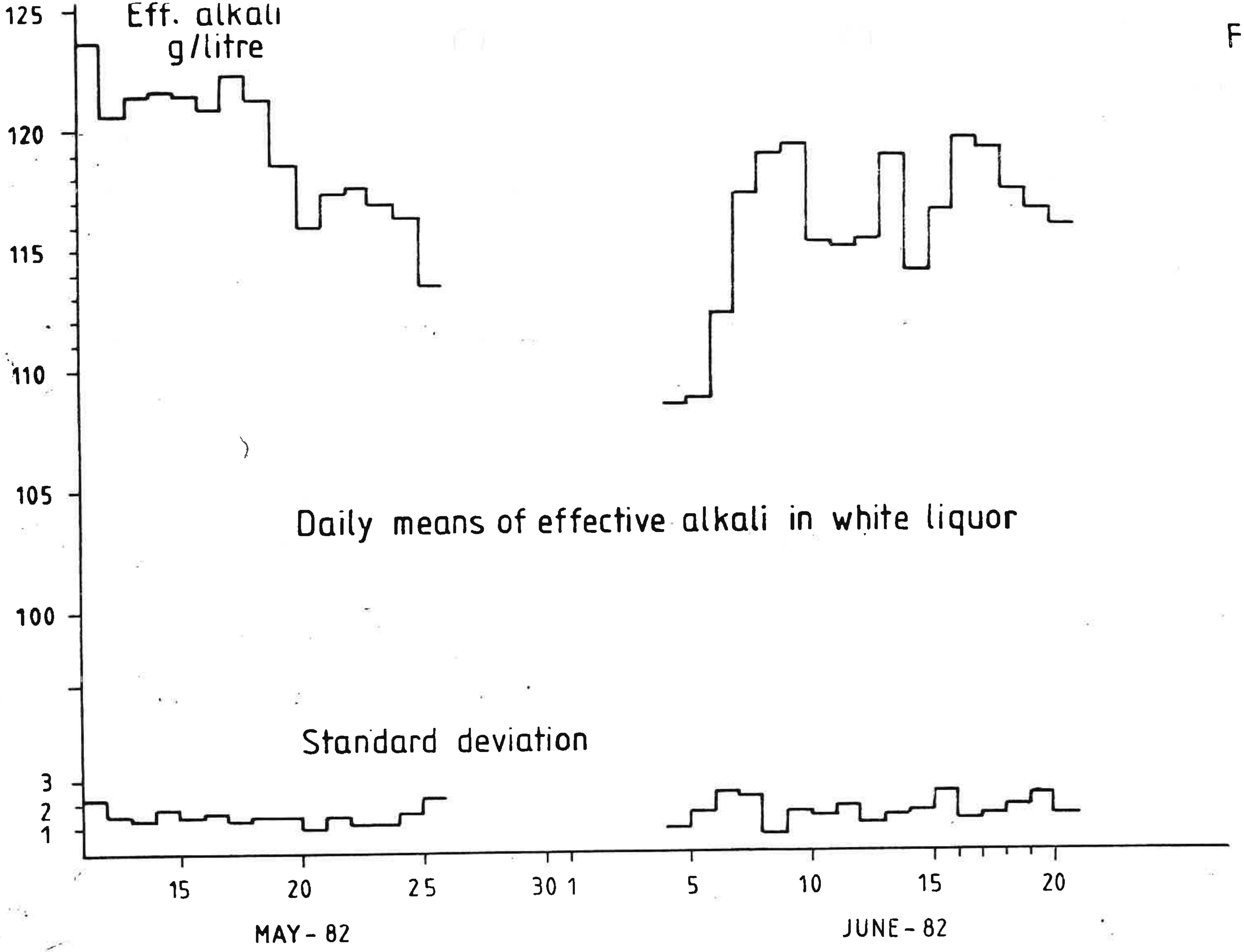
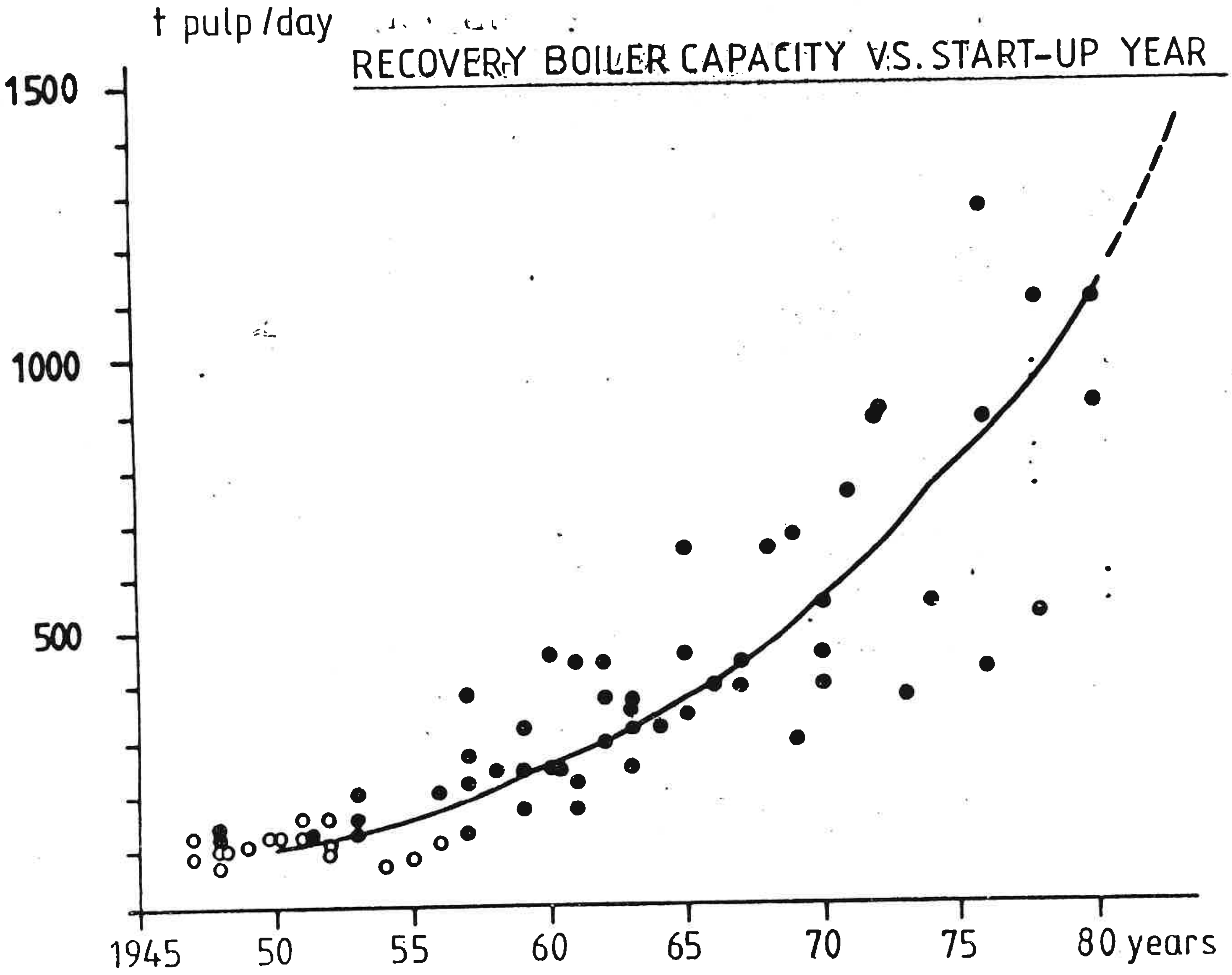
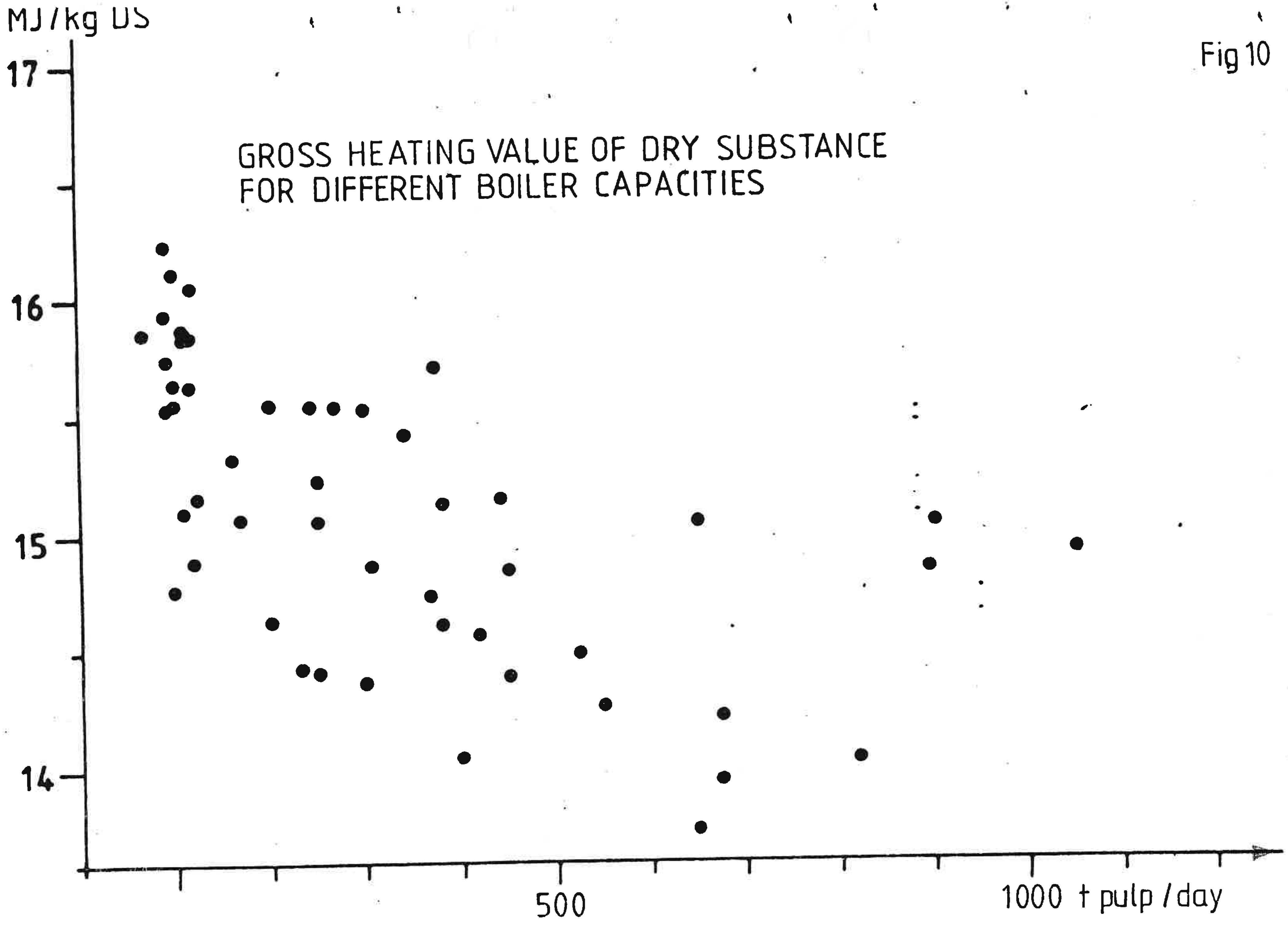

Eff. alkali
g/litre
125
120
115
110
105
100
3
2
1
Daily means of effective alkali in white liquor
Standard deviation
15
20
25
30 1
5
10
15
20
MAY - 82
JUNE - 82

Fig 9



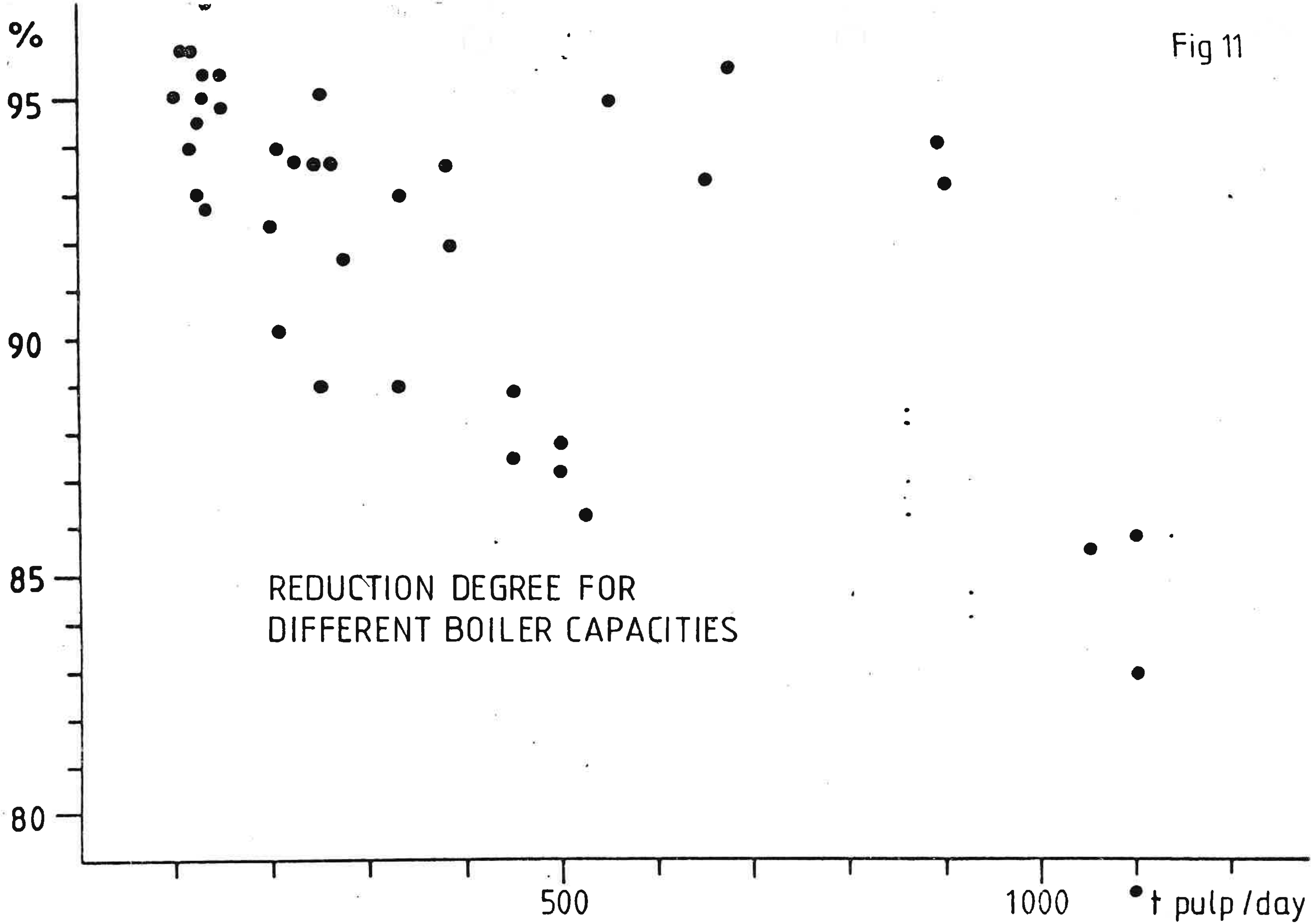
RECOVERY BOILER CAPACITY V.S. START-UP YEAR

Fig 10



GROSS HEATING VALUE OF DRY SUBSTANCE FOR DIFFERENT BOILER CAPACITIES

Fig 11



REDUCTION DEGREE FOR
DIFFERENT BOILER CAPACITIES

A SURVEY OF POSSIBLE METHODS FOR RECOVERY OF KRAFT PULPING CHEMICALS

Hans Magnusson,* M. Tech.
Björn Warnqvist, Dr. Tech.

Swedish Forest Products Research Laboratory, Stockholm, Sweden

---

*) Present address: Bycosin AB, Karlstad, Sweden

Abstract

A necessary and important part of the kraft pulping process is the recovery of the pulping chemicals. In this paper, the different possibilities 'a priori' to carry out this recovery process are examined, mainly from a theoretical point of view, based on chemical thermodynamic data. Some practical considerations and reference to current development projects are also given.

Introduction: The problem

In kraft pulping, the wood is treated with an alkaline cooking liquor containing different sodium compounds. The active components in the white liqour, sodium hydroxide, NaOH, and sodium sulfide, NaHS, dissolve most of the lignin and some carbohydrates. From the spent cooking liquor, both sodium and sulfur, as well as the energy content of the organics, have to be efficiently recovered. A proposed kraft recovery process must be judged from both these points (1,2).

Also, possible recovery processes should be viewed in light of a number of basic requirements on the kraft recovery process:

- Minimum risk for smelt-water explosions
- High thermal energy efficiency
- Small losses of chemicals - those environmentally acceptable
- Reasonable investment costs - today the chemical recovery department represents about 30 % of the total capital cost of a new kraft pulp mill
- Easy to run and control - low operational costs
- Reliable - no complicated maintenance - high availability.

Today a further point of view is the use of black liquor as a potential raw material for the production of useful organic chemicals. Besides the conventional by-products, turpentine and tall-oil, some kraft pulp mills in the future may consider production of kraft lignins or other organics. For instance, this would be one way to make use of a positive overall energy balance for the mill. In this paper we will not, however, explore this particular concept further.

Our subject is to study options for making white liquor from black liquor, i.e., ways to regenerate the active cooking components sodium hydroxide and sodium sulfide. Emphasis is placed on physico-chemical principles, not on detailed descriptions of the different technical processes.

A generalised process for producing white liquor from black liquor is shown in Fig. 1. In the conventional recovery process, the chief pretreatment and post-treatment steps of Fig. 1 are, of course, black liquor evaporation and green liquor causticizing. In an ideal process, these pre- and post-treatments might be very simple, or omitted entirely if possible. The major components of the recovery process, i.e., sulfur reduction, separation of the inorganics, and oxidation of organics to generate energy, should either be combined into one continuous process (as is done, if inefficiently, in the Tomlinson furnace), or as optimised separate sub-processes. In either case, it seems that thermal processes have to be used. Experiments with the application of electrochemical and biological methods to recovery of chemicals from black liquor are reported in the literature (3,4,5) but no successful industrial process seems likely within the foreseeable future.

Chemical equilibrium - possible processes?

The possible products of any chemical process are determined by chemical thermodynamics, i.e., equilibrium. The sodium and sulfur compounds formed from kraft black liquor at various temperatures, air/black liquor ratios, dry solid contents and compositions, may be computed using known chemical thermodynamic properties of the various possible compounds (6,7,8). The main results of such calculations are indicated in Fig. 2. This figure represents a revised version of graphs in ref. (6), i.e., regions of predominance of sulfur-sodium compounds. Note that sodium carbonate is a major product throughout this diagram. Four regions of technical interest for kraft chemicals recovery are evident.

I. $H_2S(g)$ - $Na_2CO_3(s)$: At temperatures under 600-700°C and air factor $\leq$ 90 %, sulfur and sodium form the easily separable compounds hydrogen sulfide and sodium carbonate. - Cf. the SCA-Billerud process (9), and the initial stage of Brink's process (10).

Fig. 1 General kraft recovery process

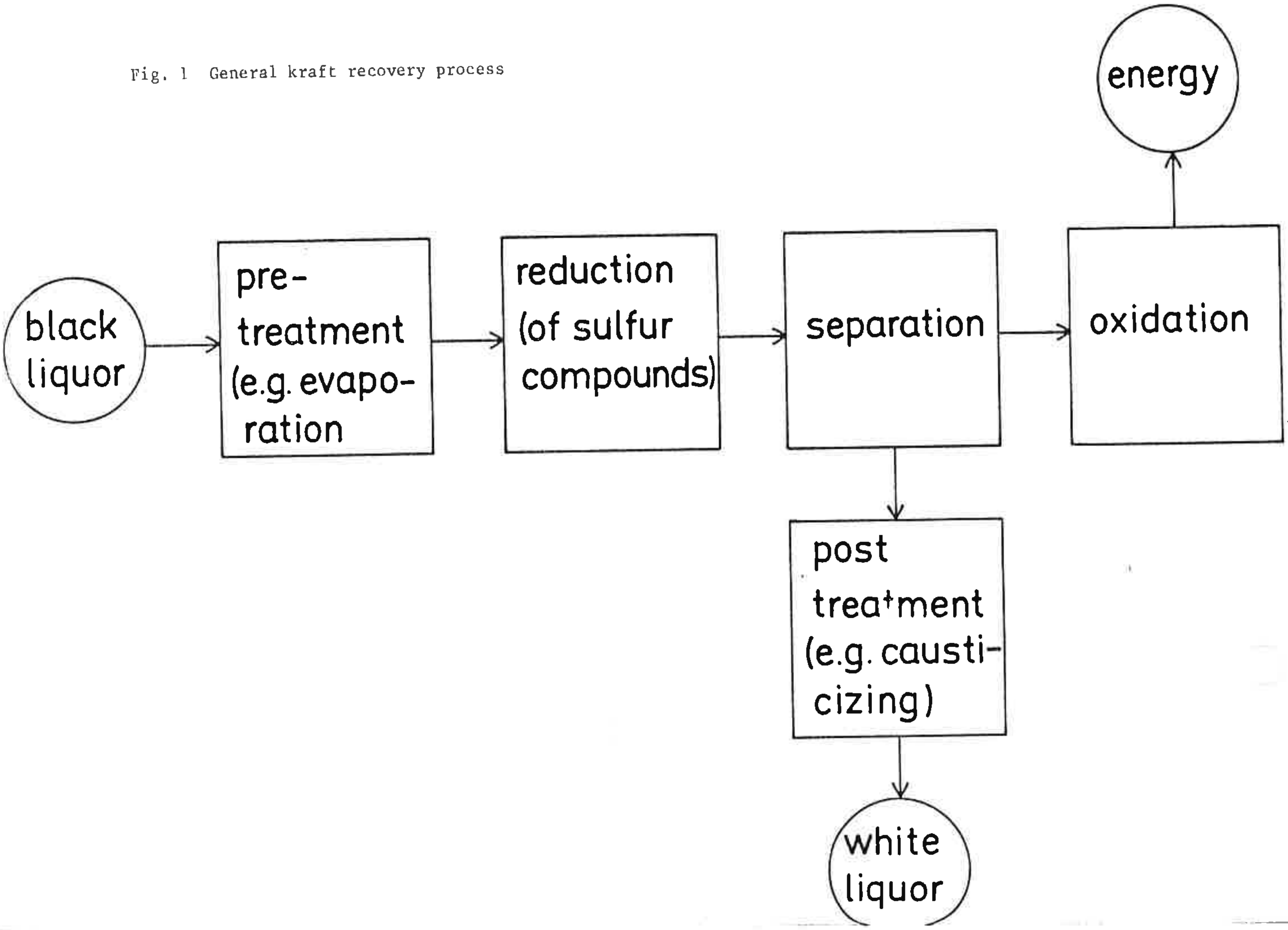
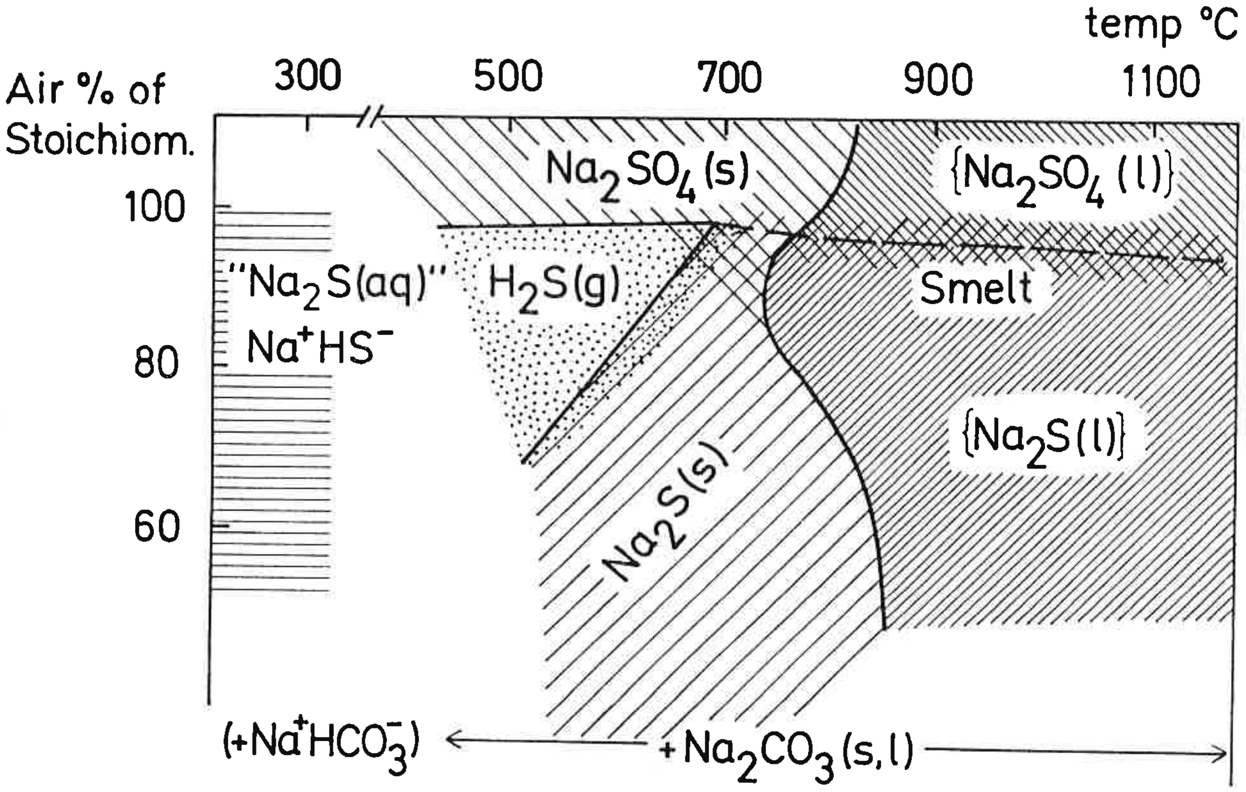


Fig. 2 Main chemical equilibrium products (S-Na compounds) from black liquor at different temperatures. (Outline).



II. Na_2SO_4(s or 1) - Na_2CO_3(s, 1): Sodium sulfate (solid or liquid) occurs at air factors $\geq$ 100 %; it must, of course, be reduced back to sodium sulfide in a separate or integrated step to be useable. - Cf. various fluidised bed furnace and related processes/proposals.

III. Na_2S(1) - Na_2CO_3(1): A liquid mixture consisting mainly of sodium sulfide and sodium carbonate, occurring at temperatures above ca. 750°C and at air factors less than ca. 90 %. - Cf. Tomlinson and other processes.

IV. Sodium sulfide (and sodium carbonate) in aqueous solution where the sulfide is stable mainly as the hydrolyzed form Na^+HS^- (aq). In order to make use of this for chemical recovery, temperature must be raised to ca. 300°C or more to decompose the organics, into char, methane and other simple compounds, more or less separable from the inorganics. Organic sulfur compounds also form, as well as some sulfur bound to the char. Obviously, a high-pressure system (typically 15-20 MPa) is called for in this option - cf. the Hydropyrolysis (11), Zimmerman (12), and Cederquist (13) processes. These processes operate with thin liquor or slightly evaporated black liquor as dictated chiefly by the thermal energy balance of the system. The applications of the two latter methods are primarily for soda liquor recovery.

Sodium hydroxide, NaOH, is not, unfortunately, a major product under any process conditions, cf. its absence in Fig. 2. Hence, the green liquor causticizing operation and the lime cycle are necessities in conventional kraft recovery. In the so-called autocausticizing processes addition of hydroxide forming components, borate (14) or certain metal oxides (15) to the system is employed.

Recovery Process technology

Within the general restrictions of chemical thermodynamics, kinetics and physical process structuring allow a certain range of technical processes. Referring to the physico-chemical outline above, a brief survey of technically developed methods, within the above areas I-III, will be given, including some comparisons with respect to energy efficiency and development status. For a more complete listing and evaluation of proposed processes the reader is referred to the literature (1,2,16).

I. Pyrolysis/gasification of black liquor into H_2S and Na_2CO_3

The SCA-Billerud recovery process for sodium based spent liquors (9) is based on this concept. It has been developed and applied chiefly for sulfite and NSSC liquors, but is applicable also to kraft recovery (2). In the latter case, the H_2S and soda formed are combined in a scrubber into a "green liquor" containing NaHS and $NaHCO_3$. Economically the process has two draw-backs. The capital cost is unfavourable for large installations. The energy efficiency is limited due to the neccessity of extracting heat from the flue-gas in two steps. The chemistry of the process deviates (favourably) from over-all chemical equilibrium due to the "fast pyrolysis" of highly atomized liquor doplets, which to a large extent act as individual "particle reactors" (17). Thus, the process is usually operated at a somewhat higher "bulk" temperature and produces a different flue-gas composition than predicted by over-all chemical equilibrium. The relative amount of pyrolytic char produced is inversely, and almost linearly, related to the "bulk" temperature. - It should be noted that in the liquor spray zone of a Tomlinson kraft recovery furnace a similar chemical reaction regime probably operates. This may be responsible for the considerable sulfur release occurring in the spray zone (18).

II. Oxidative combustion of black liquor into Na_2SO_4-Na_2CO_3(s) with subsequent reduction

A number of fluidised bed furnace concepts, operating with moderately concentrated black liquor at temperatures 700-750°C fall into this category, e.g. the Copeland/Domtar type furnace (19), the concept recently patented by International Paper (20), and other process proposals. The very desirable possibility of directly producing, sodium sulfide - sodium carbonate solids is severely limited, c.f. Fig.2, by two constraints:

- The melting point minimum for the system is 715-762°C (21), depending on the sodium sulfate content.

- The formation of considerable quantities of H_2S at temperatures in this range.

Thus, the fludised bed concept or other proposed processes, e.g. "Dry Pyrolysis" (1,2), must resort to reduction in a separate stage, e.g., the reducing zone of a recovery furnace, or in a reduction reactor using hydrogen, or char (20) as reactant.

III. Reductive combustion of (thick) black liquor into a sodium sulfide - sodium carbonate smelt

This is, of course, the main concept of the conventional Tomlinson recovery process. In a Tomlinson furnace, furthermore, the preceding steps - drying, pyrolysis/gasification of liquor dooplets and material on the "bed" surface, as well as the subsequent final combustion of reduced gases - all take place within the same furnace cavity, leading to the well known advantages and draw-backs of this recovery furnace. Other ways of utilizing this operating regime have been proposed. The "Supersmelter" is a recovery furnace recently developed by A. Ahlström Co., Finland (22). In the combustion chamber of this furnace, atomised liquor enters from the top and pyrolysis/gasification/melting occurs in suspension. Smelt is collected on a cooled set of "impactor" tubes from which the smelt gradually falls, and is finally withdrawn from the sloping furnace bottom without formation of a smelt bed. The process was initially developed for soda spent liquor recovery, but is now being operated sucessfully with kraft liquor in a pilot unit at a kraft pulp mill.

Another concept presently under development is the cyclone furnace, "NSP" (23). The ideas behind this approach are derived from knowledge about the process chemistry of black liquor pyrolysis, gasification and reduction/resulfidation, and from parallells with pyrolysis and combustion of pulverized coal.

The gasification and reduction reactions in the Tomlinson recovery furnace take place in a relatively thin layer on the surface of the bed and the velocity of the reaction is governed by the amount of air entering the layer. Similar factors govern the combustion of pulverized coal in different kinds of furnaces. Coal can be pulverized and burnt in a cyclone furnace at such a temperature that the ash is

molten and flows out of the furnace (24). The combustion load of such a cyclone is 1200-3500 kJ/m^3 s (1-3 Gcal/m^3 h) which should be compared with ca 350 kJ/m^3 s (0.3 Gcal/m^3 h) for a conventional coal-fired boiler.

Spent pulping liquor can be fired under conditions similar to those in a coal-fired cyclone, for example, the Loddby furnace for spent calcium sulfite liquor. Theoretical and laboratory studies have indicated the feasibility of a kraft recovery furnace according to the cyclone concept. The development and design of a pilot-plant NSP is now in progress as a joint Swedish-Finnish project (25). One advantage of this process, also, is the virtual elimination of the hazard of smelt-water explosions.

Energy efficiency of alternative recovery processes

Energy balances for a number of different kraft recovery processes have been published (1,16). Comparing recovery processes which are based on widely different technical principles is inherently very difficult. Strictly speaking, the entire pulp mill must be included and the boundary of the energy balance must be placed judiciously. In the comparison presented below, Table , the total energy efficiency of the system evaporation - recovery boiler - liquor preparation, including causticizing has been applied.

Table System energy efficiencies of recovery processes (high-level energy)

Conventional recovery, Tomlinson furnace	50 %
St. Regis Hydropyrolysis	50-55 %*
Recovery with NSP cyclone furnace, thick liquor (65 %)	52 %
Recovery with NSP, dry liquor (98 %)	58 %
Dry pyrolysis (Weyerhaeuser)	60 %

---

* "Greenfield" and "Incremental", respectively (11)

Comments: Firing a Tomlinson furnace with "dry liquor" would, in principle, increase its system energy efficiency, also, by 6 %. However, this would call for some design changes of the boiler. There is not yet any proven industrial process available for evaporating/drying black liquor to very high dry solids content with multiple-effect technology and economy. - The technical feasibility of the complete Dry Pyrolysis process is not yet established. None of the new process alternatives listed in the Table have been been developed as yet beyond the pilot plant stage.

The SCA-Billerud pyrolysis process, and the fluidised bed (Copeland-Domtar) process have (high level) energy efficiencies considerably lower than 50 %, with additional recovery as low-level energy.

Conclusion

It seems clear that an "ideal" kraft recovery process, by the criteria indicated in the Introduction of this paper, is not yet available - or even attainable considering chemical and thermodynamic limitations. There are a number of new kraft recovery process ideas presently in various stages of development representing all the four operating regions identified in this paper from chemical-thermodynamic considerations. It is still too early to predict which alternative - if any - will succeed the Tomlinson recovery process. This will have to be decided on the basis of techno-economical data and operating experience from pilot and industrial scale demonstration units. Combinations of processes must be considered, e.g., new types of recovery boilers with black liquor evaporation to very high dry solid contents, or with autocausticizing processes. In addition, factors outside the pulp mill recovery department will be decisive, such as the future competetiveness of kraft pulp vs. other pulps like soda-anthraquinone, chemimechanical, etc., for various paper products. Other important factors will be the future trends of energy and capital costs and, not least, present and future restrictions with respect to environmental pollution and worker safety.

References

1. Forum on Kraft Recovery Alternatives,
   IPC, Appleton, Wisc., 1976; Supplement 1978.

2. New recovery processes for black liquor,
   G. Sundblad Seminar, Skövde, Sweden, 1976.

3. T.T. Collins Jr and P.E. Shick,
   Paper Tr.J. 155(1971):1, 11-19.

4. a) E. Santiago,
      Tappi 54(1971):10, 1641-1645.
   b) A.M. Kennedy, and J.M. Jernigan,
      US. Pat. 2905604.

5. J.F. Selin and V. Sundman,
   Finska Kem.samf. Medd. 80(1971):1, 11-19.

6. T.W. Bauer and R.M. Dorland,
   Can. J. Techn. 32(1954) 91.

7. E. Rosén,
   Sv. Kem. Tidskr. 76(1964) 195.

8. B. Warnqvist,
   Sv. Papperstidn. 76(1973):12, 463-466.

9. E. Horntvedt and J. Gommi,
   Paper Tr. J. 158(1974):16, 32.

10. D.L. Brink and J.F. Thomas,
    U.S. Patent 3639111, 1972.

11. R.L. Myers and I.H. Stockel,
    1981 International Conf. on Recovery of Pulping Chemicals,
    Preprints, pp. 165-169 and refs. therein.

12. J.E. Morgan and C.M. Saul,
    Appita 22(1968):3, 60-75.

13. K.N. Cederquist,
Sv. Papperstidning 85(1982):7, 28 and refs. therein.

14. J. Jansson,
Paperi Puu 61(1979):8, 495-504;
International Conf. on Recovery of Pulping Chemicals,
Preprints, pp. 205-210.

15. E. Kiiskilä and N.E. Virkola,
Paperi Puu, 60(1978):3, 129.

16. P.J. Hurley,
Chem. Eng. Progress 76(1980):2, 43-53.

17. A. Björkman,
1981 International Conference on Recovery of Pulping Chemicals,
Preprints pp. 3-7,
1968 Symposium on Recovery of Pulping Chemicals, Helsinki,
Proceedings, pp. 235-265.

18. A. Borg, A. Teder and B. Warnqvist,
Tappi 57(1974):1, 126-129.

19. A.J. Liem andT. G. Sheridan,
1981 International Conference on Recovery of Pulping Chemicals,
Preprints pp. 223-230. Pulp & Paper Mag.Can. 83(1982):5, 79-84.

20. S.T. DiNovo and W.E. Ballantyne,
U.S. Pat. 4303469, 1981.

21. S. Andersson,
Chemica Acta, in print.
B. Tegman and B. Warnqvist, Acta Chem. Scand 26(1972):1, 413-414.

22. B. Arhippainen and E. Kiiskilä,
1981 International Conference of Pulping Chemicals,
Preprints, pp. 261-265.

23. G. Holme,
Swedish Patent No. 7204304-5,
U.S. Patent No. 3867251.

24. W. Gumz,
Kurzes Handbuch der Brennstoff und Feuerungstechnik,
3. Ed., Berlin 1962.

25. B. Warnqvist,
1981 International Conference of Pulping Chemicals,
Preprints pp. 1-2.

C1 - 1

MULTIVARIABLE CONTROL OF RECOVERY BOILERS

P. Uronen, Professor, University of Oulu, Finland
A.K. Kippo, Lic. of Technology, Oy Wärtsilä Ab,
Turku, Finland

1. Abstract

In order to study the applicability of multivariable control strategies to the control of recovery boilers a state space model based on mill experiments has been developed. The multivariable controller studies use the linear quadratic theory and it includes both feedforward and feedback controllers.

This control strategy is then used in extensive simulations and different controller structures have been compared. Some aspects and comments concerning the efficiency and real implementation of the proposed strategy are also included.

2. Introduction

The dynamics and control of recovery boilers have been quite intensively studied since the end of 60's and there are numerous articles since that published on this subject. As a result there are now several computer control system packages for recovery boiler control available in the market and also many in-house computer systems in operation. Totally we estimate today about 45-50 computerized recovery boilers in the world.

When all this work started there were two main approaches:

a) Analyzing the operation of the boilers paying special attention to disturbances and to the measurable input-output relations. Main strategy was SISO (single input - single output) with feedforward and feedback loops. The models used are quite simple and also some multivariable features (compensations), adaptive features and optimization are included.

b) Developing mathematical model for the whole process and applying modern control methods (multivariable, optimal and/or stochastic control).

So far the installed systems belong mainly in the group a) because of many practical limitations; instrumentation problems, lack of process knowledge and models etc. and the published results have been very positive /1, 2, 3, 4, 5, 6/. But also a lot of ambitious modeling studies have been published during the last 10 years /7, 8, 9, 10, 11, 12, 13/. The more extensive use of these and other larger models has not yet started. We could caal the existing RB computer systems the systems of first generation and we must look further possibilities to improve them. As already stated one important restriction and limit has been and will be the measurements, and when new sensors will be developed especially for the on-line analyzing of the BL quality and for the direct measurement of the state variables of the bed and furnace one problem still remains: how to use and utilize this new information in the control system? The recovery boiler process is difficult control objective for many reasons; the basic character of the process, the complicated interactions and large dimensions of the equipment just to mention some of them. This leads us to the theory of distributed multivariable control. But using models with distributed parameters would certainly lead to unpractical solutions and thus we can divide the whole process in different sections or zones with lumped parameters and this is a more practical starting point for multivariable control of the whole RB process.

3. Model building

For model building purposes the process variables were grouped according to Fig. 1 /11/. The experimental work was made at the Aanekoski Mill of Metsaliiton Teollisuus Oy, Aanekoski, Finland. The boiler data is given in Table 1 /11/. For identification step tests were used. The step changes in the input variables among the normal operating point and all the measurable response variables were logged. During this phase the process was controlled manually with the analogue backup. The measurement interval used was 72 seconds.

The following step change sequences in the input or disturbance variables were analyzed separately:

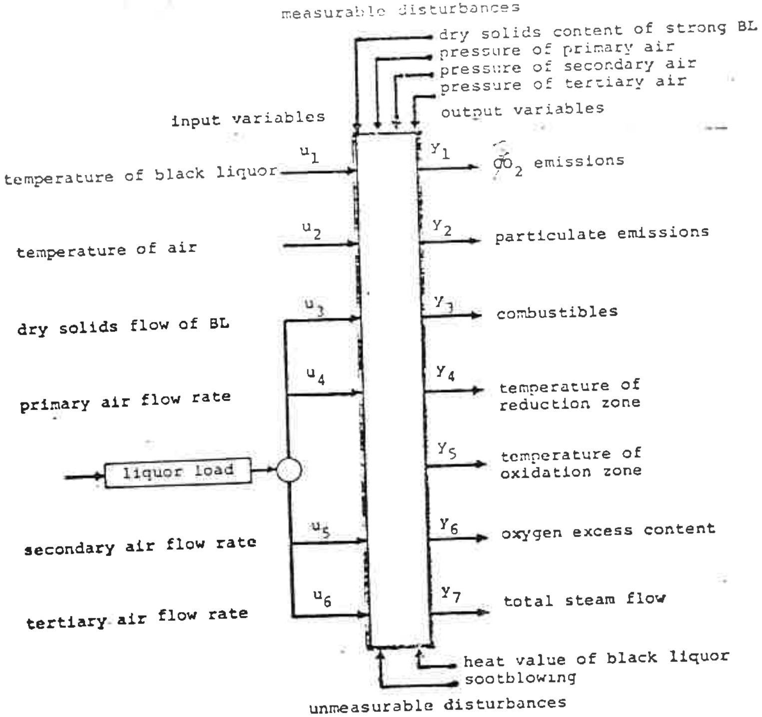


FIGURE 1. Variables of the model /11/.

TABLE 1. Boiler data /11/.

	Operation point	Dimension	Direct measurement	Computed	Computation was based on	Step change	Process variable
Black liquor: temperature	119	C	x			±2C	u_1
pressure	0.62	bar	x			+0.08ba	u_3
flow	0.0077	m^3/s			x		
Dry solids content	62	%	x				v_3
Dry solids flow	6.40	kg/s		x		-0.4kg/s	u_5
Auxiliary oil flow	0.0	m^3/s					
Total air flow	10.3	m^3/s			x		
Primary air flow	10.6	m^3/s	x		x	±0.5m^3/s	u_2
Secondary air flow		m^3/s			x		
Ratio of secondary/ tertiary air	2.6	-		x		-0.7	u_6
Primary air pressure	9.3	mbar		x			v_1
Secondary air pressure	10.8	mbar		x	x	+0.7mbar	v_2
Temperature of air	145	C	x				u_4
Temperature of reduction zone	1068	C	x	x	x		y_4
Temperature of oxidation zone	978	C	x	x	x		y_5
Oxygen excess content	3.5	%		x	x		y_6
SO_2-emission	0.073	%	x	x			y_1
Particulate emission	11.3	g/m^3	x				y_2
Combustibles	0.1	%	x				y_3
Total steam flow	23.8	kg/s		x			y_7
Main steam flow		kg/s			x		
Steam flow for sootblowing		kg/s			x		
Out blowing		kq/s			x		
Sootblower		-	x				

- changes in primary air flow rate
- changes in the ratio of secondary/tertiary air flow
- changes in secondary air pressure
- changes in dry solids flow
- changes in black liquor temperature
- changes in black liquor pressure.

In each sequence the effect of all the input and disturbance variables on the output variables were identified. The parameters of the model were computed by a recursive least squares method and partly by a recursive maximum likelihood method using the interactive program package IPSI.SISO /14/ which package was at the disposal of this research in the UNIVAC 1100/22 computer of the University of Oulu.

The identification is based on a linear time-invariant difference equation

$$y(k) + a_1 y(k-1) + \ldots + a_m y(k-m) = b_1 u(k-1-d) + \ldots + b_m u(k-m-d) + v(k) \qquad (1)$$

Here

$y(k)$	is the output variable (deviation from the stationary value)
$u(k)$	is the control variable
m	is the order of the model, $m = 1,2,3,\ldots$
$d = T/T_o$	is the lag of the model, $d = 0,1,2,\ldots$
T	is the dead time of the process
To	is the sampling time
$v(k)$	is an unmeasurable disturbance.

Equation (1) can be put into the vector form

$$\underline{y}(k) = \underline{x}^T(k)\underline{\beta} + \underline{v}(k) \qquad (2)$$

and here

$$\underline{x}^T(k) = |y(k-1) \ \ldots \ y(k-m) \ u(k-1-d) \ \ldots \ u(k-m-d)| \qquad (3)$$

$$\underline{\beta} = |-a_1 \ \ldots \ -a_m \ b_1 \ \ldots \ b_m|^T. \qquad (4)$$

According to the least squares estimation method with N observations the error function to be minimized is

$$V = \underline{e}^T\underline{e} = (\underline{y}-\underline{W}\underline{\beta})^T(\underline{y}-\underline{W}\underline{\beta}) = \sum_{k=m+d}^{m+d+N} \underline{e}^2(k) \qquad (5)$$

Here

$$\underline{W} = \begin{vmatrix} -y(m-1-d) & \ldots & -y(d) & u(m-1) & \ldots & u(0) \\ \vdots & & \vdots & \vdots & & \vdots \\ -y(m+N-1+d) & \ldots & -y(N+d) & u(m+N-1) & \ldots & u(N) \end{vmatrix} \qquad (6)$$

and the estimates for $\underline{\beta}$ will be

$$\hat{\underline{\beta}} = |\underline{W}^T\underline{W}|^{-1}\underline{W}^T\underline{y}\ , \ \text{if } N \geq 2m \qquad (7)$$

and the expectation for $\hat{\beta}$ is

$$E\{\hat{\underline{\beta}}\} = E\{|\underline{W}^T\underline{W}|^{-1}\underline{W}^T\underline{W}\underline{\beta} + |\underline{W}^T\underline{W}|^{-1}\underline{W}^T\underline{e}\} \qquad (8)$$

If the latter term in equation (8) is zero i.e. $\underline{e}$ and $\underline{W}^T$ do not correlate with each others and the error has zero mean we will get a true value for model coefficients as the expectation.

This method can be improved by using more and newer measurements or by the recursive equations. The equation (7) can be presented in the recursive form

$$\hat{\underline{\beta}}(k+1) = \hat{\underline{\beta}}(k) + \underline{K}(k+1)|\underline{y}(k+1) - \underline{x}^T(k+1)\hat{\underline{\beta}}(k)| \qquad (9)$$

and here

$$\underline{K}(k+1) = \{1/|1+\underline{x}^T(k+1)\underline{P}(k)\underline{x}(k+1)|^{-1}\}\underline{P}(k)\underline{x}(k+1) \qquad (10)$$

$$\underline{P}(k+1) = |1-\underline{K}(k)\underline{x}^T(k+1)|\underline{P}(k) \qquad (11)$$

$$\underline{y}(k) = |y(1) \ y(2) \ \ldots \ y(k)|^T \qquad (12)$$

The initial values for the recursive algorithm can be obtained from the non-recursive solutions or they can freely be chosen.

The aim of this identification was to find the parameters of the model which are as simple as possible and accurate enough to reliably describe the dynamical behaviour of the process. Based on these facts the order of the model was chosen to be one and the delay to be zero. The choosed form of the model (1) was thus

$$y_i(k) = -a_1 y_i(k-1) + b_1 u_j(k-1), \quad i=1,\dots,7, \quad j=1,\dots,6 \qquad (13)$$

The three disturbance variables were noticed using the same form. This choice made the model rather stiff. On the other hand this kind of model should not be very sensitive for measurement noise. The overall state space model was composed of MISO-models and it was in the form

$$\underline{y}(k+1) = \underline{\Phi y}(k) + \underline{\Delta u}(k) + \underline{\Omega v}(k) \qquad (14)$$

The elements of the variables $\underline{y}$, $\underline{u}$ and $\underline{v}$ are presented in Table 1 /11/.

4. Design of a multivariable controller

The next step was to apply the above model for designing a multivariable controller suitable for recovery boiler. First a simple multivariable proportional feedback controller was designed by using linear quadratic control theory. The basic design equations here are:

$$\underline{u}(k) = \underline{G}(k)\underline{y}(k) = \begin{bmatrix} g_{11} & \cdots & g_{1m} \\ \vdots & & \\ g_{m1} & \cdots & g_{nm} \end{bmatrix} \begin{bmatrix} y_1(k) \\ \vdots \\ y_m(k) \end{bmatrix} \qquad (15)$$

and objective function:

$$J = \frac{1}{2} \Sigma \, [\underline{y}^T(k)\underline{Qy}(k) + \underline{u}^T(k)\underline{Pu}(k)] \qquad (16)$$

and recursive formulas:

$$\underline{G}(k) = -\underline{P}^{-1}\underline{\Delta}^T\underline{S}(k) \qquad (17)$$

$$S(k) = \phi^{-T}[\underline{R}(k) - \underline{Q}] \, , \; \underline{R}(0) = 0 \qquad (18)$$

$$\underline{R}(k) = \underline{Q} + \phi^T[\underline{R}^{-1}(k+1) + \underline{\Delta P}^{-1}\underline{\Delta}^T]^{-1}\underline{\phi} \qquad (19)$$

It can be shown that this design procedure will always give a stable solution. The tuning of this controller can be carried out by eigenvalue tests or by simulations when small changes in setpoints (reference values) will be given. Then we have

$$\underline{u}(k) = \underline{G}(k) \, [\underline{y}(k) - \underline{r}(k)] \qquad (20)$$

where r(k) is the change of the set point vector. For the closed loop we will get

$$\underline{y}(k+1) = [\underline{\phi} + \underline{\Delta G}(k)]\underline{y}(k) - \underline{\Delta G}(k)\underline{r}(k) + \underline{\Omega v}(k) \qquad (21)$$

This equation can now be used in studying the closed loop behaviour under various circumstances. When the statistical values of the disturbances are known the feedback characteristics can be studied for different changes in the set point vector.

The feedforward term from the measurable disturbances can be noticed by augmenting the equation (20) into the following form

$$\underline{u}(k) = \underline{G}(k)\{\underline{y}(k) - \underline{r}(k)\} - \{\underline{P}^{-1}\underline{\Delta}^T(\underline{\Phi + \Delta G}(k))^{-T}\underline{R}(k)\underline{\Omega}\}\underline{v}(k) \qquad (22)$$

It would be advantageous to know the disturbance beforehand in order to be able to diminish the disturbance amplitude before it occurs. However this is in general very difficult because feedforward control will not always give good results for constant disturbances. Better results are often achieved increasing the integral term into the control law. In this case the control law is

$$\underline{u}(k) = \underline{G}(k)\{\underline{y}(k) - r(k)\} + \underline{G}_I(k) \sum_{i=1}^{k} (\underline{y}(k) - \underline{r}(k)) + \underline{G}_v(k)\underline{v}(k) \qquad (23)$$

This is commonly called to the multivariable PID-control law. The general block diagram of the structure of the multivariable system is in Fig. 2.

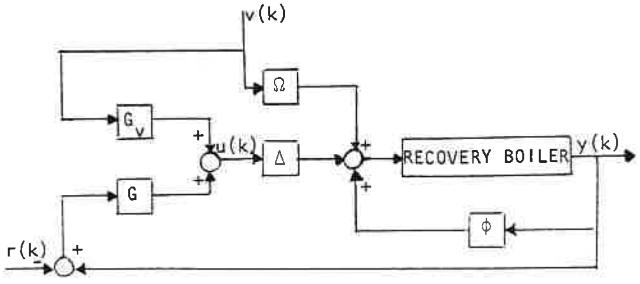


FIGURE 2. Block diagram of the multivariable system.

5. Discussion

The simulation results revealed many interesting correlations which were earlier observed experimentally.

The temperature of black liquor is used as the manipulated variable. Variations in black liquor solids content and kinematic viscosity can be compensated with it. It has be an immediate influence in the pressure of black liquor to be compensated for, on the furnace temperature levels and on SO_2 and particulate emission. However black liquor boiling point can not be exceeded due to the difficulties in handling the drop size in spraying.

Dry solids content is used as an immediate input variable and indirectly it will affect many other variables. However the variations in dry solids content disturb the process and they should be compensated before spraying for example by controlling the temperature of incoming black liquor accordingly. Increasing dry solids content affects the black liquor drop size distribution thus causing changes in the combustion process and the temperature levels. Increasing the dry solids flow adds the fuel power fed into the furnace. This leads to higher temperature of oxidation zone, as seen in Fig. 3.

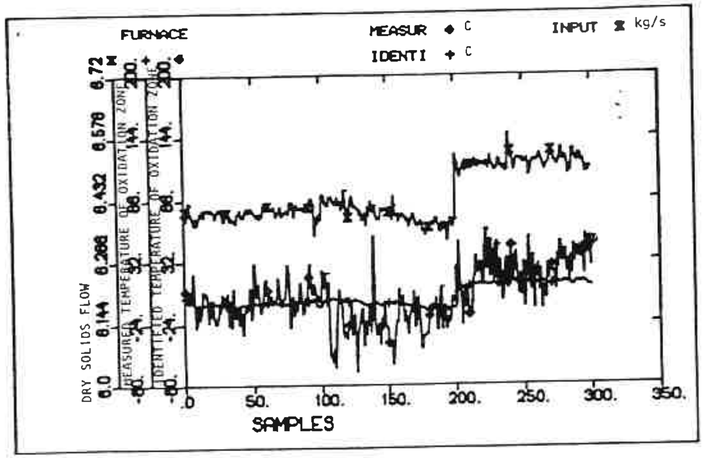


FIGURE 3. Measured and identified temperature of oxidation zone with zero mean when dry solids flow has been used as an input variable.

The main target of the multivariable control has been to stabilize the operation despite of disturbances. Simulated changes in reference values have also been carried out. Fig. 4. shows the simulation results with multivariable controller when the set point values of SO_2 emission, O_2 content and combustibles in flue gases were set 5 % below the normal operational point. As can be seen the controller works very well.

The studies concerning the sensitivity and real application of the above control strategy are continuing.

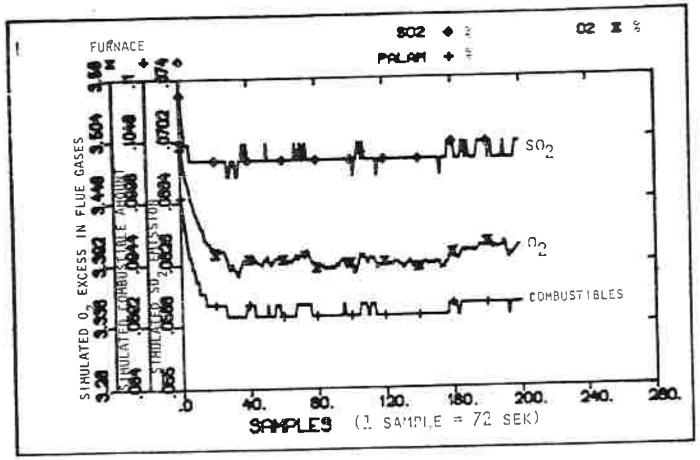


FIGURE 4. Simulation results with multivariable controller. The set point values of SO_2 emission, O_2 content and combustibles in flue gases are 5 % below the normal operation points.

6. Conclusions

The recovery boiler process is a very complicated chemical process of great economic importance and with some potential risks in its operation. Therefore in the automation and control of it the safety, reliability and up-time requirements come first. It is thus very understandable that the implementation of very sophisticated control strategies has so far been excluded. Before applying such strategies careful studies, experiments and tests must be carried out. The modelling and design methods applied here seem to be

8. CHAMBERLAIN R.E. and WOSTRADOWSKI K.A., Key to recovery boiler preformance is understanding of variables, Pulp and Paper, March 1979, pp. 96 - 101.

9. GALTUNG F.I. and WILLIAMS T.J., A mathematical model of a recovery furnace, Modeling and control of kraft production systems, ISA, 1975.

10. KIPPO A.K., Simulation studies of dynamics and multivariable controllers of the recovery boiler, Tech. Lic. Thesis, Division of control Engineering, University of Oulu, 1979.

11. KIPPO A.K., OJA T.J.O. and URONEN P., Multivariable controller applied to recovery boiler and to pilot-plant continuous casting process, (in Finnish), Automaatiopaivat 81, Helsinki, Finland, 1981.

12. KIPPO A.K., URONEN P. and JUTILA E.A.A., Identification of the recovery boiler, First IASTED Symposium on Modelling, Identification and Control, Febr. 1981, Davos, Switzerland.

13. TARVAINEN H. and TINNIS V., On process models for a kraft recovery boiler and their utilization for computer control, International Instrumentation-Automation Conference & Exhibition, New York City, USA, 1974.

14. KAARIAINEN S., Identification program package IPSI.SISO, (in Finnish), Report 33, Department of Process Engineering, University of Oulu, 1979.

OY KAUKAS AB: A PRIME EXAMPLE OF COMPUTER BASED RECOVERY BOILER CONTROL

by

P. Simola, Research and Development Manager, Power Division,
Oy Kaukas Ab, Finland
K. Kaski, Account Manager, Energy and Recovery Applications,
Measurex Oy, Finland
R. van Winkle, Marketing Manager, Energy, Measurex International
Systems Ltd, United Kingdom

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

OY KAUKAS AB, A PRIME EXAMPLE OF COMPUTER BASED RECOVERY BOILER CONTROL

Pertti Simola, Research and Development Manager, Power Division,
Oy Kaukas Ab, Finland

Kalevi Kaski, Account Manager, Energy and Recovery Applications,
Measurex Oy, Finland

Richard van Winkle, Marketing Manager, Energy,
Measurex International Systems Ltd

1. ABSTRACT

Recovery Boiler is the most expensive single unit in chemical circulation of sulphate process and generally remains the bottleneck in production after incremental investments in other mill departments aiming at increasing production level. Recovery of chemicals and heat generation in Recovery Boiler consist of several different functions.
A computer control system installed above normal instrumentation level in control hierarchy is succesfully used to optimize the operation of the recovery process. Economical results can be measured by regeneration capacity increase, thermal efficiency increase, soot-blowing steam decrease and reduction efficiency increase.

2. INTRODUCTION

Oy Kaukas Ab is one of the most integrated wood processing mills in Finland. It is located between Lake Saimaa and the Russian border in the eastern part of Finland. There are four plants on the same site. They are a plywood mill with a capacity of 35,000 m3 per year, a sawmill with a capacity of 330,000 m3 per year, kraft mill producing totally bleached hardwood and softwood pulp with a capacity of 300,000 tons per year and a LWC paper mill with a capacity of 300,000 tons per year.

At the end of 1979 it was decided to purchase computer control systems for the two Recovery Boilers and two Evaporator lines in use at the mill. The Measurex systems started their trial run in 1980 and finished their evaluation in 1981.

The main targets of the project were to increase liquor firing capacity and to improve energy usage. The improvement of energy usage was to be done by optimizing excess air and by decreasing soot-blowing steam consumption.

The savings achieved by the control systems cannot be attributed to any single control function. The optimization control and human effort combined give the end result.

Briefly the results are:

- about 5 % throughput increase in liquor firing, which enabled 15,000 tonnes more pulp to be produced per year.

- 20 % decrease in sooth-blowing steam consumption on a long term basis. During the first 6 months after system start-up, there was a 30 % decrease in soot-blowing steam.

- 1 % to 1,5 % reduction of oxygen on RB1. No reduction was possible on RB2 without a boiler construction change.

Reduction efficiency for both Recovery Boilers is about 96 to 98 per cent.

3. PROCESS

3.1 Evaporator Plant

The evaporator trains are located in the Recovery Boiler House, while causticising and lime kilns are in the pulp mill a hundred meters away. The first evaporator is made by Enso-Gutzeit. It has six effects and a capacity of 42 kg H20 evaporated per second. The second Evaporator is made by Rosenlew. It has also six effects, but has a capacity of 30 kg H20 evaporated per second.

Hardwood black liquor is fed into the first Evaporator in effects 6 -2. Half strong liquor dry solids content coming from stage two is 48 %.

Softwood black liquor is fed into the second Evaporator in effects 6 - 2.

Hardwood and softwood black liquors are mixed together in the half strong liquor tank. Number one stages of the evaporators are used as concentrators, but without forced circulation. The mixed half strong liquor is fed through one of the first effects while the other one is being washed. The target final product has 59,5 - 60 % dry solids content.

3.2 Recovery Boilers

Both Recovery Boilers are equipped with three air zones, but the construction differs.

RB1 is a CE type boiler with primary air ports 1 meter from the furnace bottom and the secondary air ports are located 3,4 meters up from the primary air ports. Liquor firing guns are just above the secondary zone and tertiary air ports are 4,6 meters above the secondary air ports.

RB2 is CE/Ahlström type. The primary air ports are 1,15 meters from the furnace bottom, secondary air ports are 1,2 meters above the primary ports. The distance between the secondary ports and liquor guns is 3,8 meters and the tertiary ports are 6,2 meters above the secondary ports.

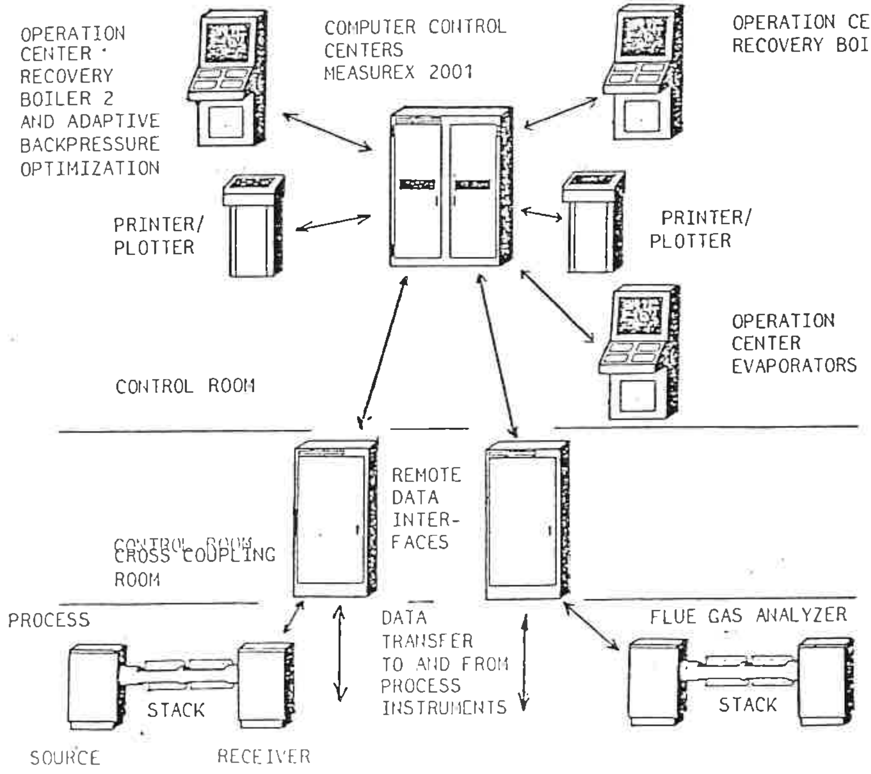
Mixed softwood/hardwood black liquor is fired with a stationary plate nozzle guns. RB1 has 6 guns and RB2 has 2 guns on nominal production levels.

Main design data	RB1	RB2
Manufacturer	SMV	Ahlström
Type	CE	CE
Start-up	1964	1971
Capacity norm/max	640/720 tds/day	410/460 tds/day
Steam pressure	80 bar	80 bar
Steam temperature	480 °C	480 °C
Steam generation	30/33 kg/s	17/19 kg/s
Number of soot-blowers	54	28
Process computer	Measurex 2001	Measurex 2001

4. MEASUREX PROCESS CONTROL SYSTEMS

Two Measurex process control computer systems are in operation at Oy Kaukas Ab. One system controls RBI and both Evaporators and the other one controls RB2 and optimizes the back pressure steam network. The systems are equipped with semigraphic colour video operator systems and report/alarm graphic printers.

Two Measurex 2225 Flue Gas Analysers are used to obtain in situ measurements of CO, CO2 and SO2. Every eight hours, the computer automatically standardises the Analysers using calibration gases.



4.1 Controls

The main function of the computer control system is to economically optimize process operations.

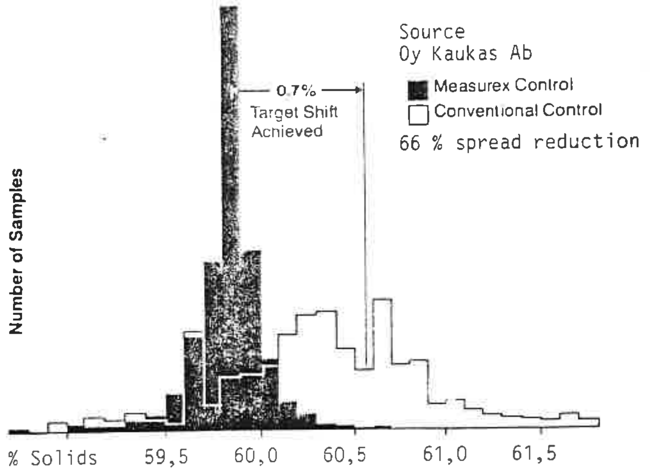
In the Evaporator process this means that Evaporator combination is optimized to run at its maximum capacity with available steam and black liquor quality. The strong black liquor solid content target is tightly maintained while maximizing black liquor throughput.

In the Recovery Boiler process, this means that furnace conditions are optimized giving a stable char bed, an optimal temperature profile, a reduction in particle carryover from liquor spraying nozzles and a minimum of energy losses. The optimal temperature profile results in high reduction efficiency, improved dust quality and reduced stack losses. Soot-blowing steam is minimized by soot-blowing only when needed. High quality dust makes this necessary less often. These optimized furnace conditions make a higher firing rate than before possible. Since Oy Kaukas Ab was bottlenecked by the Recovery Boilers, this meant an increase in pulp production. The maximum firing rate constraints were selected keeping pulp production and Recovery Boiler operation at their most cost effective point.

4.2 Main Evaporator Control Functions

- Evaporation rate control by three possible ways either
  - feed liquor flow target
  - weak liquor tank level
  - maximum available steam
- Dry solid content control, by steam adjustment or by liquor throughput, (steam limited)
- Evaporation optimization control
- Washing optimization control

Evaporator Steam Limited
% Solids Variation Reduction



4.3 Recovery Boiler Controls

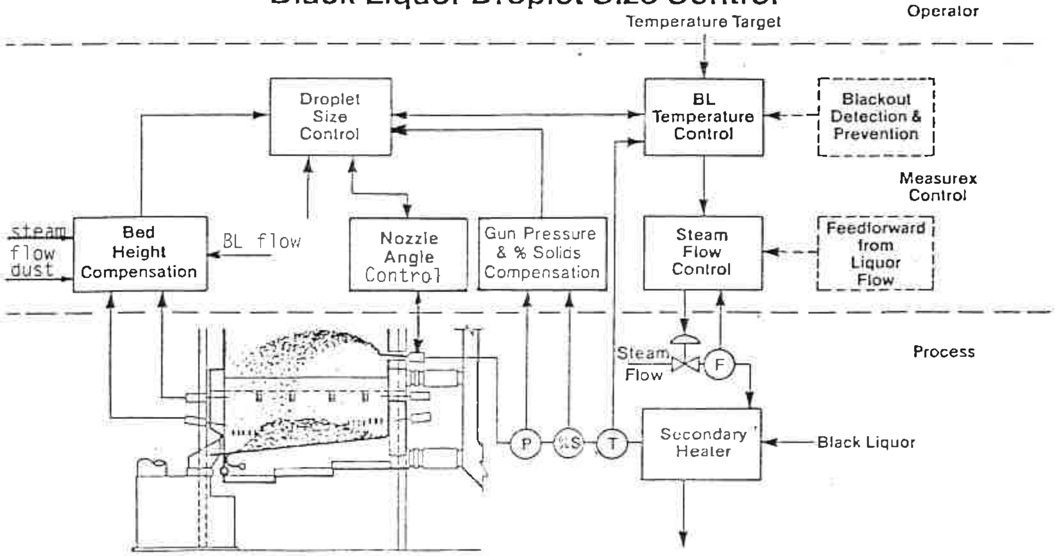
The base for control in a Recovery Boiler is to optimize the furnace temperature profile and stabilize the char bed. A Process control system achieves this goal in two ways. These two ways are liquor firing optimization and air distribution optimization.

The process control system changes liquor temperature and the angle of the liquor guns to compensate for firing rate changes and black liquor quality changes.

The computer calculates the liquor temperature target using a multivariable model. Firing rate, nozzle pressure, dry solids content, furnace temperatures, furnaces emissions and steam flow rate are used in the model. The target for the liquor gun angle is determined by a model based on firing rate and dry solids content. An adaptive search control is used to optimize nozzle angle around modelled target on RB1.

A software module called Blackout Detection and Prevention keeps track of the process on a long and short term basis. It provides the models with necessary information about process changes. It also reacts quickly to act against blackouts.

Black Liquor Droplet Size Control



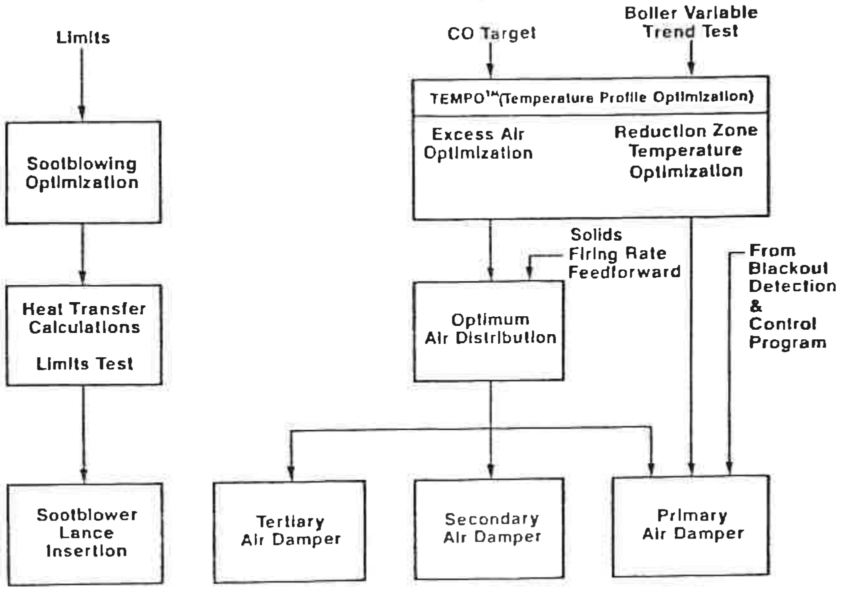
Air Distribution Optimization

Two control programs are used to optimize the air distribution in the furnace. The excess air optimization control uses secondary and tertiary airs to control excess air. The adaptive optimization program uses a search algorithm to regulate the distribution between primary and secondary/tertiary airs. TEMPO is the product name for these controls.

TEMPO uses long and short term process histories for the search algorithm. Main variables used are SO2, dust and furnace temperatures.

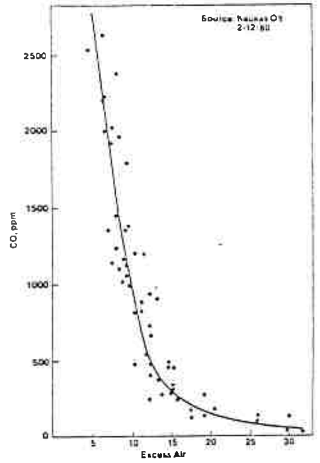
The basic air distribution is maintained using a combustion model. The allowed control range for air distribution optimization is determined for each air zone. These control ranges are more limited on RB1 than RB2. This is because the relative distance between primary and secondary zones is different for each boiler.

Thermal & Chemical Efficiency Optimization



Excess Air Optimization

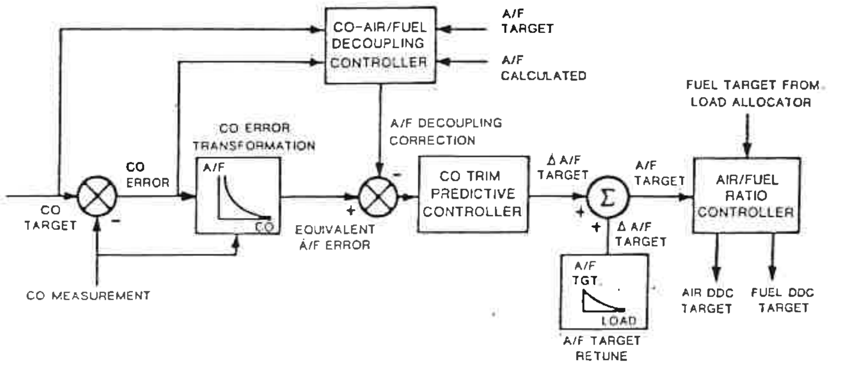
Recovery Boiler CO vs. Excess Air



The process control system optimizes excess air based on a carbon monoxide feedback. Process dynamics in terms of transport delays and time constants and process gain in terms of the CO-air transformation curve are determined for each boiler. The CO target is determined based on the stack gas loss vs unburned fuel loss. The target is normally between 200 to 500 ppm.

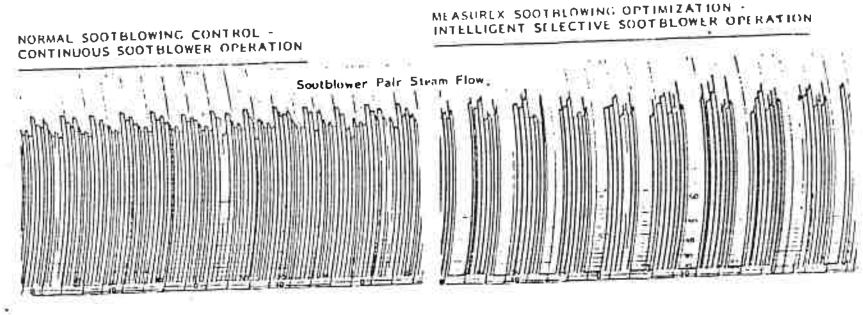
An algorithm which searches for optimum CO and O2 or optimum CO and CO2 to obtain minimum stack gas loss is used at Kaukas. The result of the algorithm is the optimum CO target.

Carbon Monoxide Control



Soot-blowing Optimization

The process control computer activates soot-blowing when and where needed. A contact output is given for each pair of lances. The need to activate soot-blowing is determined from heat transfer coefficients, stack gas pressure drops and time. Optimized furnace conditions gained through smelt bed stabilization and temperature profile optimization help to decrease soot-blowing.



Throughput Optimization

The firing rate target is determined either by operator entry on the video, or by the throughput optimization program. The throughput optimization program automatically selects firing rate target based on key variables and constraints. Some examples of these variables are strong black liquor inventory, cooking liquor inventory and ID fan amperes.

The optimization control sets the target for the liquor line pressure. The control range for line pressure is 0.55 to 1.0 bar while the pressure of the nozzles varies from 0.3 to 0.65 bar.

.ion.

5. Summary

Installation of the process control computer systems on two different types of Recovery Boilers was justified by good results. The savings potential was realised without major construction changes of the boilers. Process knowledge was improved among operators and project engineers alike. These intangible savings have not been estimated.

The best guarantee for long term success is a positive attitude from the operators. This was achieved in two ways at Oy Kaukas Ab. First meetings between project engineers and operators were held at an early phase of the project. These meetings served to inform the operators and to learn about their experience with the process. These meetings were held on a regular basis from inception until completion of the project. Secondly, the computer control systems provide safe and stable operation of the Recovery Boilers and Evaporators. This results in a high confidence level of the operators.

An on line process control computer system is an excellent tool for process experiments and control development.

STATIONARY FIRING OF RECOVERY BOILER

by

O. Pantsar
Enso-Gutzeit Oy, Imatra, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August
September 1, 1982

C3 - 1

STATIONARY FIRING OF RECOVERY BOILER

Ossi Pantsar
Enso-Gutzeit Oy, Imatra, Finland

1. Abstract

Plenty of research and practical work has been done on black liquor recovery boilers. Boiler construction and opinions of how the furnaces should be run have been and still are amazingly varying and incompatible. However, the basic phenomenons remain unchanged. They cannot be overlooked. It must be everyone´s interest to strive for the one and only truth. Is it the one expressed herein or something else, can be discussed but - there ought not to be many.

2. Introduction

The basis of everything below is the experience through real cases that comprises of - can be said - whole scale of liquor spraying patterns, furnace sizes, shapes and air feed arrangements. The cases are impossible to deal with individually within the frames of this presentation. The principles will be outlined in comparison between four different manners of firing.

To make the matter more concrete the real names are used. There is no intention to put the mentioned boiler manufacturers into any superiority order. What is wrong with the firing of each of them will be said and improvement suggestions are given.

The main types of recovery furnaces are the CE and the BW. Combinations of those exist. The Tampella boiler is included as an example of exceptions. Air and liquor feed arrangements differ from each other. Also, boiler constructions and sizes are represented in a large selection.

That, in fact, reflects either an uncertainty on how the furnaces should be designed and operated or a will to make differences in a commercial purpose.

3. CE - Firing

An ordinary CE boiler has air ports at only two levels and 6 to 16 oscillating liquor guns. The primary air ports are located one to one and a half meter above the furnace bottom. The liquor nozzles are about four and half meters up from the primary air feed and the secondary air ports are about three meters above the liquor guns. The secondary air ports are located so that the air into the furnace is fed tangentially in order to create a vortex for a good mixing of gases.

The vertical distance between the primary and the secondary air ports is large. The normal air distribution is 70 % of primary and 30 % of secondary air. This tends to give a low bed and cool the bed area and the lower furnace with large local excess of air which makes it necessary to use a fine liquor spray. The fine spray promotes entrainment which causes the combustion to take place from the bed to almost the boiler bank. If the primary air ratio were reduced to say, 50 % the bed sides would get hotter. However, the lower furnace at the drying region would be cold because of insufficient air and weak combustion. The upper furnace tends, in this case, to be hot because of the effective heat release during the secondary combustion. Also a reduction of primary air may cause a very abrupt build up of the bed.

The liquor guns are oscillated vertically to eliminate effects of poor spraying and to spread the liquor over the bed region. Because of the fine spray and the gun oscillation the CE boilers have heavy carbon carry over and consequently a tendency to clog. Cool or missing bed does not emit sufficiently of Na-gases when sulphus oxide emissions are high. Also the pH of salts tends to be low. Reduction of salt cake is relatively low.

The upper furnace of the CE boiler is too hot under a normal or overloading conditions.

The CE liquor nozzle gives a cone shaped spray. The lower portion of the spray goes two to three meters below the upper portion. Such a wide spray especially with the oscillation, is insufficient for the formation of the desired combustion zones as discussed later. When the gun is in its low position the lower spray goes straight to the bed as wet and in up position the upper spray goes steeply upwards toward upper furnace. There is no shape in getting the precise zones, see chapter 6.3. The CE furnace is shown in the figure 1.

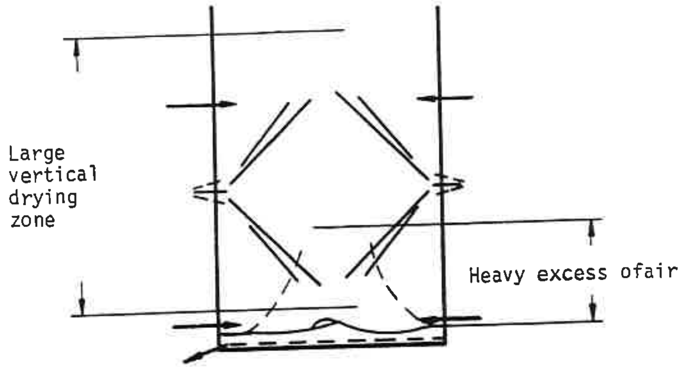


Figure 1. CE-furnace.

4. BW - Firing

The BW boiler has usually three air feed levels and 1 or 2 liquor nozzles. The primary air ports are one to one and a half meters from the bottom, the secondary air one to two meters from the primary air feed and the tertiary air feed is two to three and half meters above the liquor gun(s). The guns are located on the elevation about three meters above the secondary air feed.

A special feature of the BW boiler is the wall drying and burning. The liquor is sprayed with high pressure (high velocity) so that most of it is deposited on the walls to dry.

Splash plate nozzles are used. The nozzles are located on
walls. They are oscillated in both the vertical and

tions. Thus the liquor is spread evenly around the walls of the furnace. The liquor char hangs on the walls between the secondary and the tertiary air registers.

When the liquor has dried it falls down in front of the primary air ports. The primary air is adjusted to control the rate of burning. It also blows some char up onto the bed. Steep and uneven side surfaces of the bed obstruct the smooth penetration of the primary air.

The BW boilers have bad carbon carry over caused by the very effective gun oscillation and high liquor velocity. The temperature conditions in the lower furnace are not acceptable. A complicated gun oscillation system gives a lot of maintenance work because sealing questions have not been solved satisfactorily.

The heat transfer is deteriorated by the isolating char layer on the furnace walls which, on part, keeps the upper furnace hotter. Heavier TRS emissions are favored by the cool walls underneath the char. The sloping bottom and a poor process conditions in the periphery of the lower furnace cause difficulties with the smelt spouts. A large portion of the bed is often dead and sticky. The hot zone above the bed is not utilized in liquor drying. The BW boiler is shown in figure 2.

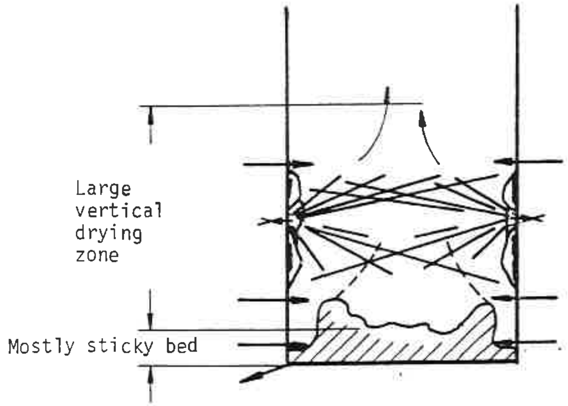


Figure 2. BW-furnace.

5. Tampella Boiler

The Tampella boiler uses roughly BW gun oscillation and the BW guns. The biggest special feature is the location of the secondary air feed in relationship to the liquor feed. Those namely are very close to each other. The secondary air feed level is about one third of a meter above the liquor feed. Thus the bed cannot be controlled by the secondary air. The secondary air is fed straight into the steam vapor liberated from the drying liquor or even liquor itself is sprayed very steeply upwards straight to cold air. No doubt, desired zoning is incurably lost. Hard to imagine any benefits from this arrangement. The theories behind are unknown. Tampella boiler is shown in figure 3.

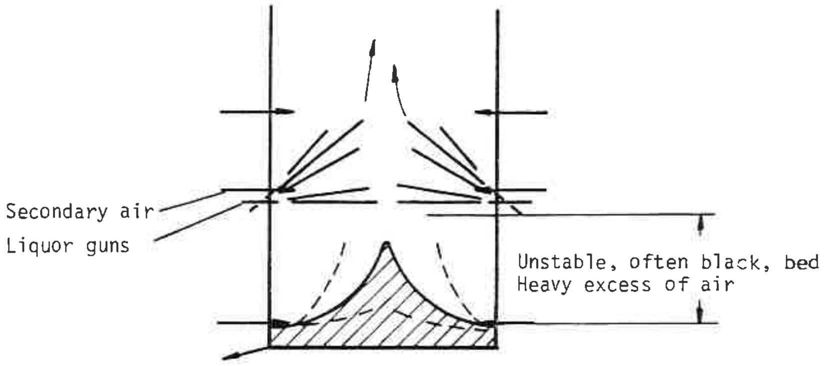


Figure 3. Tampella furnace.

6. Stationary Firing

6.1 Liquor Nozzles

The aim of the stationary firing is the highest firing rate of the lower furnace. It starts with the proper liquor spraying. The stationary liquor nozzles are of plate type with an extremely simple construction. The nozzle is shown in figure 4.

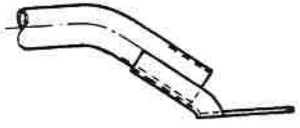


Figure 4. Stationary firing liquor nozzle.

The best liquor droplet size control and spray pattern is obtained with a low velocity splash-plate nozzle. See figure above. Exact geometry of the nozzles is chosen according to the arrangement of the air feeds, the points of the liquor feeds, the boiler size and shape. It even can be questioned what is the standard nozzle suitable for any of the very "unstandardized" furnaces.

The spraying process itself is common with other plate nozzles, but also differences are clear. Arguments for use of this kind of gun with steel hose connections are: better load control using black liquor pressure 1), better droplet size control 2), good size distribution 3), better drying of black liquor droplets 4), freedom from plugging 5), long lifetime of nozzle 6), homemade style - low cost 7) and improved safety 8).

6.1.1 Better Load Control Using Black Liquor Pressure

There are two opposite factors in spraying. When the pressure of black liquor is increased the droplets tend to get smaller.

Simultaneously, the flow and amount of black liquor increase and that tends to increase the size of the droplets. Thus, it can be concluded that small changes in black liquor pressure do not have a very strong influence on the size of droplets. Possible slight changes in droplets size can be corrected by the viscosity control. The area is roughly 25...30 % of maximum load. The need of changing the number or size of the nozzles has almost been eliminated in practice.

On the other hand, there is a certain automatic control for flying distance of droplets with an increase in furnace firing rate.

The pressure and the velocity increase, but also the temperature in the furnace rises accelerating the drying. Flying distance does not lenghten.

6.1.2 Better Droplets Size Control

The temperature of black liquor can usually be kept close to its boiling point. This prevents flashing and uncontrollable spraying as is often found with CE firing. On the other hand, the liquor must not be dispersed violently with too high velocity, BW version. The most important factor in a atomization of black liquor is the viscosity, not the pressure. The pressure itself is only an auxiliary factor needed for velocity. Liquid black liquor does not expand or get compressed.

The thickness of the black liquor film as it crosses the edge of the distribution plate depends on the viscosity of the liquor.

Viscosity is controlled with liquor temperature keeping the solids constant.

6.1.3 Good Size Distribution

A correct geometry of nozzles guarantees the proper droplet size distribution. The main factors are the angle between the tube and the plate, the distance between the tube and the plate as well as the shape and the size of the plate.

6.1.4 Better Drying of Black Liquor Droplets

A narrow size distribution of liquor droplets is necessary for good drying in the furnace. No wet drops must fall onto the bed. When the spray is flat and horizontal the drying zone vertically is the shortest possible.

If the size distrubution is large, the temperature must be set too high to prevent big drops falling onto the bed as wet which causes the smaller droplets to be too fine and to be carried upward into the boiler section. As a result of this: black liquor drying takes place in every elevation from the bed up to the upper furnace. None of the required zones - reduction, oxidization and drying-exist.

6.1.5 Freedom from Plugging

The nozzles have no interior parts or ports. With approp
nozzles the holes of nozzle tubes are large enough to st

Clogging does not take place and cause any fluctuation or pressure changes in the black liquor firing if the liquor temperature is kept low enough and the location of the gun in its opening is correct.

6.1.6 Long Lifetime of Nozzles

The dimensions of the nozzle tubes are constant while liquor travels from the hose to the plate. The liquor velocity is uniform with no discontinuities or dead spots. Cooling is thus effective and no overheating of tube material caused by radiation occurs resuming that the conditions are as stated above.

6.1.7 Homemade Style - Low Cost

The construction of nozzles is simple. There are only three parts welded together. The material is carbon steel. The nozzles can easily be fabricated in the mill shop. The cost is very low.

6.1.8 Improved Safety

The above conditions insure good and steady firing and thus they improve safety. Steel hose connection without oscillation is safer than any other alternative.

The stationary nozzles are of course not oscillated. An oscillation would destroy the zone formation and impair the draft control.

6.2 Air Arrangement

Because there are a large number of different kind of air feeds and so forth, it is not possible to say here what would a stationary firing be like in each separate case. Therefore, the matter will be described in a should-be-manner.

The primary air feed in all boilers is fairly good, in general. There should be a possibility to control the primary air penetration regardless of the flow in certain extent.

The secondary air feed should not be much above the maximum functioning bed, see reference. In principle it means one to one and a half meter from the primary air feed. That does not depend upon the size of a

furnace but on the other hand, it does. Namely, a liquor drop does not know whether it is in a small or a big furnace. However, because of the longer spraying distance the secondary air jet tends to expand vertically requiring more space. Wet liquor spray and cold secondary air must not meet each other. That is why the distance between the primary and the secondary air feed, as well as between the secondary air and the liquor feed must accord with the area of the furnace cross section. Also, the vertical air distribution is subject to the area of the furnace cross section.

The secondary air feeds are needed on only the two opposing walls. When the boiler is big - wall length more than eight meters - some ports would be useful to have also in the center of the other walls. This is to avoid crossing air flows which may wholly destroy the smooth gas service in the lower furnace and keep the corners heavily over aired and cold. Thus a part of an expensive furnace bottom area is being lost.

The design of the secondary air ports should be so that the air penetration is effective. The number of the ports should be large enough to give an even and solid air cover over the furnace cross section. This is roughly valid with also the tertiary air feed. Symmetry of the upper furnace is difficult to control with vortex (CE).

6.3 Furnace Process

Let us imagine that the boiler in question is an average sized, 800 to 1 000 tonnes per day solids. Design is as described above. The liquor spraying is performed with four or six stationary nozzles located on the side walls. Liquor supply and gun installation are symmetric. Each gun provides a liquor flow varying depending on the firing rate between two and two point seventy-five litres per second. The liquor solids are close to 64 %. It might be anything from the accepted low limit up to 70 or so, but a range from 62 to 66 has proven to have been the most suitable. The more difficult liquor - including low solids - the more important it is to do as suggested below. The liquor temperature is a function of desired viscosity. The furnace and its zones are presented in figure 5. The furnace bottom is 8x8 m^2. Other dimensions are in right relationship to the wall dimensions.

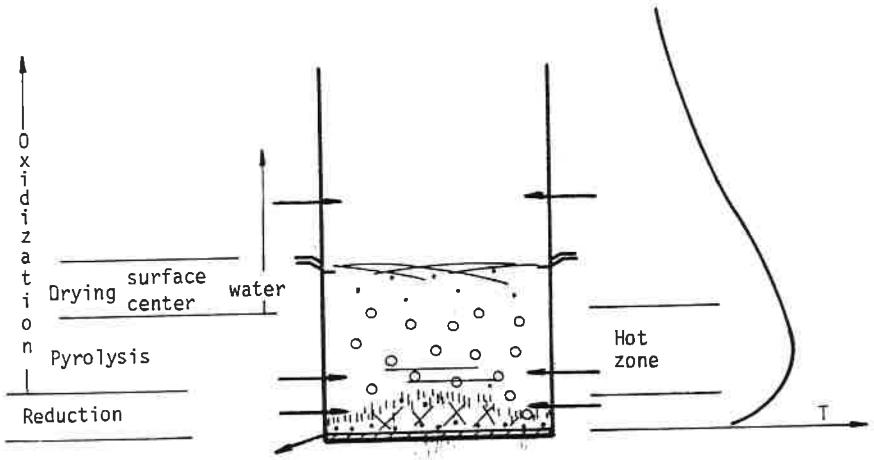


Figure 5. Stationary process zones.

6.3.1 Drying

When a liquor drop is introduced into the furnace its temperature begins to rise, then follows a water evaporation from the surface of the drop that is followed by center drying and rapid expansion which makes the drop light and porous. This stage is very important because the aerodynamic proportion of the drop changes dramatically. Now the orbit in the furnace is mainly defined by gas movements.

6.3.2 Dry Distillation (Pyrolysis)

The dry distillation of carbohydrates follows the water escape. Released gases ignite. The burning gives heat accelerating the release of volatiles. The drop loses its mass and starts to collapse, finally dropping down onto the bed. Apparently, the density of the drop is at its lowest right prior to the collapse. So, it is easy to conclude that the most important thing is to fix the stage in which the drop meets the bed because the quality and functioning of the bed is definitely depending on that stage.

6.3.3 Char Bed

The drop in the bed now contains chemicals from the cooking and carbon. Carbon burns taking O_2 from air and from Na_2SO_4 forming CO_2 and furthermore Na_2CO_3. Sodium sulphate (Na_2SO_4) reduces into Na_2S. Of course, there are countless number of other reactions also taking place.

The combustion of the residual carbon and the reduction of sodium sulphate is dependent upon the partial pressure of oxygen in the gases above the bed as well as their turbulence and the temperatures of the bed and gases. A high temperature and sufficient carbon favor good reduction. A high temperature also favors rapid combustion of carbon and fusion of the smelt (i.e., an active bed as opposed to an inactive or sticky bed). A sticky bed tends to cool off and build up.

The temperature of the bed is increased by a radiation from the hot zone above it. In turn, the hot bed releases combustible gases into the zone. The hot zone above the bed insures the complete drying of the falling liquor droplets. Moisture leaves up in time not cooling the most intensive oxidization region.

6.3.4 Primary Air

The primary air is used to trim the periphery of the bed. It also (penetrating the bed and reacting at the bed surface), contributes to the heat release.

6.3.5 Secondary Air

The secondary air "burns" the gases emitted by the bed and pyrolysis of the liquor after the drying. It maintains a high temperature in the "hot" zone.

The primary and the secondary air together form the cover underneath which there is a space for the bed.

6.3.6 Tertiary Air

The tertiary air is used in completion the combustion and to provide a small excess.

It must be guaranteed that too much air is not fed even locally into the lower furnace. To meet this requirement the tertiary air flow may be relatively high. It can be supposed that even in the best cases a certain portion of the fuel burns at or above the tertiary air feed elevation. If that portion is, for example, 20 % of total fuel, then 20 % plus excess of total air should be fed through the tertiary air feed. About 30 % of the total air. In the case of less tertiary air and more secondary or primary air, the part of air consumed after the tertiary air feed is taking part only in cooling of the lower furnace. In addition to this the extra gases from down worsen a carry-over of char.

The burning is to be accomplished as far down as possible.

6.3.7 Total Air and Air Distribution

The total air should not significantly exceed that required for complete combustion. Any air, fed into any point in the furnace space, must not exceed the quantity needed at the point. This is to guarantee the highest possible temperature and the most effective utilization of the lower furnace. It also often leads to pretty large proportional share of the secondary air.

The primary air is only effective over a narrow band around the periphery of the furnace. A relatively low velocity and amount are thus adequate. The secondary and the tertiary air must penetrate and provide a good turbulence. The pressure needed depends on the design of the air nozzles and also on their size.

6.4 Results

What is this all for? Now the liquor spraying system works properly. The droplet production is under control. The liquor solids are at the optimum for a hot and porous bed. The air distribution is good both vertically and horizontally. Extra cooling air is not present anywhere. The temperature in the lower furnace is in its maximum. Tight zoning is maintained.

When the temperature of the lower furnace is in maximum then there is:
- less carbon carry-over; less clogging
- cool upper furnace, no sticky salt; less clogging
- higher pH of salts; less clogging of economizer and precipitator
- less of oxidized and reduced sulphur emissions due to hotter bed and hence higher Na-emission from the bed (not from the stack)

- higher reduction of sulphates
- better steaming efficiency due to cleaner boiler and down concentrated combustion
- reduced soot blowing steam consumption because of cleaner boiler and more easily removable deposits
- undisturbed boiler operation
- and an advantage above all - as a consequence of all above - improved solids throughput

7. Conclusion

The stationary firing - not adopted by any boiler manufacturer so far - seems really to be an option to think about. Even though it is not enough just to push the stop button of the oscillation system very minor measures may give great benefits. Basic features of the stationary firing include at least liquor feed system modifications and often a readjustment of the air distribution with the existing equipment. When seeking all available results also the above outlined other requirements have to be fulfilled in a general way still without any exceptions from the stationary firing philosophy.

Reference
Ossi Pantsar: "Controllability of Bed Reactions and Survey of Control Strategies", Eucepa Symposium, Stockholm, Sweden, May 11-14, 1982.

.id
-he

.ie recovery
the last processes
sive research

COMPUTER CONTROL OF RECOVERY BOILER - SUCCESSFUL EXPERIENCES AT FINNISH PULP MILLS

Raimo Sutinen, Erkki Telimaa and Simo Koski
Advanced Forest Automation, Oulu, Finland

1. Abstract

The first computerized recovery boiler control system went on-stream in Finland in 1975-76. At that time it was still quite a common point of view that it is practically impossible to reliably control a recovery boiler by computer. These opinions proved soon to be invalid and today there are more than 30 computer control systems for recovery boilers around the world. The experiences with the systems have been encouraging. The main benefits have been higher capacity, decreased soot-blowing steam consumption, smelt reduction increase, thermal efficiency increase and decrease of emissions in flue gas. This is achieved by optimal liquor burning and furnace temperature profile control and optimal soot-blowing sequence.

2. Introduction

A recovery boiler is one of the most expensive and most critical unit processes in a pulp mill. It also often makes the production bottleneck,and the burning process of black liquor is quite sensitive to various external and internal disturbances. A good and stable control of the recovery boiler is therefore of primary importance.

Taking into account the great importance of the recovery boiler, it is surprising that it is one of the last processes to be computerized. In 1970-73 an extensive research project concerned with the control of recovery boilers was carried out in Finland /1.2/. The first installation project was started in 1974 by Nokia Electronics, Enso-Gutzeit and the University of Oulu, and the system was in full operation at the beginning of 1976 /3/. Today 13 of the Autorecovery systems have been sold for different types of boilers. These include systems for both sulphate and sulphite processes.

3. Basic criteria for optimal recovery boiler control

The recovery boiler has a dual function: the digesting chemicals must be regenerated, and the heat released in burning the organic substance of the black liquor must be used for steam generation as efficiently as possible. The operation of the recovery boiler also has a considerable effect on the pollution of the environment.

Recovery furnace operation is a very complicated process and correct and accurate information about it is difficult to obtain. However, during the basic research and development work, and with installations of the Autorecovery systems some basic criteria for optimal control were found. These criteria must of course be empirically tested and tuned at real process conditions for every individual boiler during the control system start-up period.

The most important parts of the control system are: liquor spraying and bed control, air controls, and heat recovery and soot-blowing controls.

4. Liquor spraying and bed control

The main problem in burning black liquor is to have and continuously maintain a sufficiently high combustion temperature. All efforts must be directed toward controlling

this problem. This means that the burning must take place at the lower part of the furnace having the temperature level there at maximum. The optimal furnace temperature profile is good for bed reactions, boiler heat efficiency, emissions and fouling of heat surfaces as well.

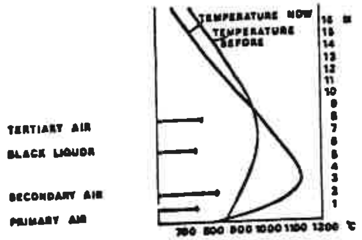


Fig. 1. Temperature profile in the furnace

The strong black liquor must be sprayed into the furnace so that the average drop size is large without cooling the bed. The most important factors affecting the drop size are: BL solid content, BL analysis, BL temperature, BL pressure and construction of liquor guns and nozzles. The correct drop size can be determined from furnace temperatures and flue gas measurements. The BL temperature is used as the manipulated variable, and experiences with the Autorecovery system show that it can effectively be used to control the location of the combustion in the furnace together with optimal air distribution control.

Porosity of the char-bed is extremely important in its proper functioning. Liquor drops that are too large will not be dried before arriving at the bed. This causes bed cooling and increase in SO_2 and H_2S emissions and finally may cause a black-out. Liquor drops that are too small cause burning to occur in the upper furnace, and will bring burning particles up in the gas stream. This is unfavorable for boiler fouling and thermal efficiency as well.

5. Air control

There are several things which should be taken into consideration with optimal air distribution of a boiler. The most important facts here are: first the boiler type and construction and then boiler load, BL quality, make-up flow, char-bed conditions, boiler temperature profile and O_2 and combustibles in the flue gas.

When using three level air distribution the following main strategy is used. Combustion in the primary air zone must be maintained at such a degree that the largest possible mixture of combustible gases rises from the char-bed to the secondary air zone. If the primary air flow is too low, the temperature will decrease causing a black-out. If, on the contrary, the primary air flow is too high, it will burn the char bed out, and the proper conditions for sodium sulphate reduction are not achieved. In order to stabilize the char-bed conditions unnecessary changes in primary air should be minimized.

The secondary air will burn the gases rising from the bed. The secondary air should have a pressure higher than the primary air to ensure a good penetration into the center of the furnace. As a result temperatures in and immediately above the bed are maximized.

The tertiary air will ensure that the combustion will be complete and that the optimal excess oxygen content in the flue gases will be reached. The combustion reactions must be brought to termination as near the tertiary air level as possible. The pressure of tertiary air must be high enough to guarantee a complete mixing in the upper part of the furnace.

The optimum air distribution as a function of BL load must always be tested empirically for each boiler. In the control strategy, the variations in BL feeding are taken into account in a feedforward manner, and feedback is taken from a compute

burning ratio (i.e. the ratio of the combustible material fed into the furnace to the amount of it actually burning) and flue gas measurements.

Measurements used in the flue gases are: excess O_2, combustibles ($CO+H_2$), dust and optionally SO_2. The combustibles measurement is prefered instead of CO because recovery boiler flue gas contains also H_2 and cannot be ignored as a consumer of oxygen /4/. Also the CO to total combustibles ratio varies depending on the excess air and boiler load level and also on black liquor quality. The total combustibles level can therefore be high even if the CO level is low. This kind of problems can be avoided by using a combustibles measurement together with a O_2-measurement. So the excess air control of a recovery boiler is a typical multivariable control block.

6. Blocking of the boiler

Blocking of the boiler is caused by particulate emissions, and because of this the temperature is very critical. If the temperature of flue gases is higher than the smelting point of inorganic compounds (e.g. Na_2SO_4 and Na_2CO_3) the layers settled on the heat exchange surfaces are very difficult to remove. Free sulphur dioxide in the flue gas decreases the pH of the salts, which in turn increases the amount of salts sticking on the tubes. It is evident that the optimal method is to bound SO_2 chemically, which means that a little more salt is generated. However, dust emissions are not increased because of reduced flue gas volumetric flow (optimal excess air control and lower flue gas temperature), which improves the efficiency of precipitators.

As a result salt accumulates more slowly and the deposits are more easily removed. Additional benefits are obtained when sootblowing is performed only when necessary.
The Autorecovery system observes the changes in the measured or calculated criteria in the different sections of the

boiler. When one of the criteria reaches its limit, sootblowing of the group in question starts. Typical groups consist of superheater, boiler front, boiler rear and economizers.

7. The Autorecovery system

The main purpose of the Autorecovery system is to maintain conditions in the furnace so as to optimize the regeneration of cooking chemicals in the black liquor and to keep the heat surfaces clean so as to ensure optimum utilization of heat for steam generation.

A typical system includes the following control functions (Fig. 2).

- BL load control
- BL spraying control
- BL temperature control
- total air flow and air distribution control
- control of temperature profile and symmetry in the furnace
- excess air optimization
- fouling monitoring and sootblowing optimization
- emission control and monitoring
- production maximization
- reporting & alarming

In addition, there exist several additional features, which can be included in the system; such as draft control, control of direct contact evaporator, dissolving tank control (TTA control), control of additional fuels etc. The system includes especially such functions which can directly or indirectly affect burning reactions in the furnace, effective heat transfer and minimization of emissions. A typical option of the Autorecovery is also the control of evaporation plant - the Autovapor system.

The system includes versatile reporting facilities. Alterations and further developments can be made flexibly and without any special programming in most cases, so that changes can be made by mill personnel. Reports are available for different history levels and reported values are typically computed specific and efficiency numbers. Also different statistics, maintenance reports, graphical trends and flow charts and MIS reports are sometimes included in the system.

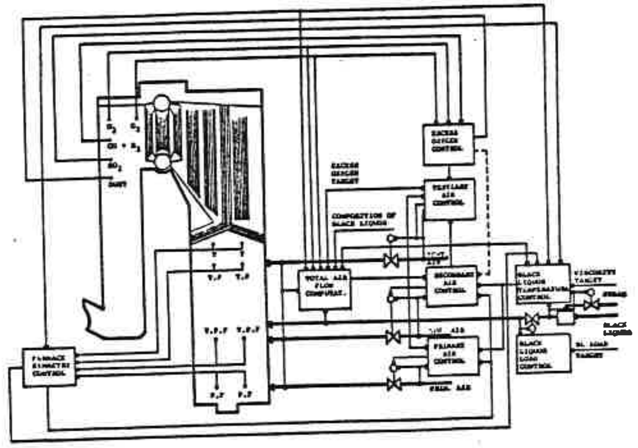


FIG. 2 Autorecovery control system

8. Mill experiences

The first Autorecovery system was installed seven years ago and today there are experiences with ten installations. The systems have been installed for CE, BW and Tampella boilers with different capacities and constructions. Both hardwood and softwood liquors are burned. Also the first system for sulphite liquor recovery boiler has been installed

The experiences show that the payback time of the system is less than one year. The main areas of the benefits are: increased capacity, decreased soot-blowing steam consumption, higher smelt reduction degree, higher boiler thermal efficiency and lower emission level. Savings can also be achieved with lower auxiliary fuel consumption and other energy savings, slower corrosion rate of the boiler and better reporting and supervising system. Typical numbers of the benefits with the Autorecovery systems are shown in Table I.

TABLE I

THE AUTORECOVERY SYSTEM BENEFITS

CAPACITY INCREASE	2 - 6 %
(WITH BOILER MODIFICATIONS	15 - 20 %)
SOOT-BLOWING STEAM DECREASE	18 - 40 %
REDUCTION DEGREE INCREASE	1 - 7 %-UNITS
THERMAL EFFICIENCY INCREASE	1 - 3 %-UNITS
- FLUE GAS TEMPERATURE DECREASE	10 - 63 °F
- EXCESS OXYGEN CONTROL	0,4 - 1,5%-UNITS
EMISSIONS DECREASE	
- SO_2	3000 PPM
- H_2S	30 - 90 PPM

Because the recovery boiler is a very expensive process unit, it also often makes the production bottleneck in a pulp mill. And because the capital costs of a pulp mill are very high, quite a lot of effort should be directed to increase the bottleneck department capacity. In these cases the main goal of the Autorecovery system is the production capacity maximation. It is possible that some units can be even 10 per cent overloaded on the annual basis with the help of the computer system, optimal boiler operation and better process know-how. It can be verified that the production of the discussed mills is not limited by their recovery boilers. In these cases the payback time of the system is very short.

With optimal liquor burning control and optimizing the soot-blowing intervals significant savings in sootblowing steam consumption are achieved. This is generally supported by the reduced number of shutdowns required for total water washings or manual cleaning of the clogged boiler. Additionally, the existing deposits are easier to remove.

The basic idea in the soot-blowing control is that the conditions in the furnace must be controlled so that increasing the salt deposits is minimized and their quality kept not sticky. This is achieved with optimal char-bed conditions and boiler temperature profile. The rest of the benefits are achieved, when soot-blowing is started only when soot-blowing criteria indicate that one part of the heat transfer surfaces has been fouled.

The experiences indicate that soot-blowing steam consumption can be reduced as low as 2 - 3 % of the steam generated. The potential depends on the boiler configuration, boiler load level and soot-blowing system configuration.

The smelt reduction degree of Na_2SO_4 has generally been increased with the computer control projects. The meaning of computer control is that it keeps the circumstances in the char-bed stable and optimal for good reduction. The potential of better control depends of course on the starting level. The savings are coming mostly from reduced dead load of the liquor circulation, which means energy savings (in the evaporation plant and recovery boiler) and also some chemical savings. The value of these savings can be hundreds of thousands of US dollars/year in larger mills.

The increased thermal efficiency of the boiler comes from lower flue gas losses. This is achieved with optimal excess air level and lower flue gas temperature.

The tightening regulations for environmental load have also set limits for emissions of the recovery boiler. Also certain savings of the make-up chemicals can be achieved if the emissions can be decreased. With the correct air distribution, liquor spraying and temperature profile in the boiler H_2S and SO_2 emissions will be minimized. In a recovery boiler with no cascade evaporator there will be found no or only very little H_2S or SO_2 in the flue gases with optimal control.

Other savings, like e.g. lower corrosion rate of the boiler, are not so easily calculated in money, but these can be very significant, if this means a longer lifetime for a boiler.

9. Conclusions

A recovery boiler is one of the most expensive and critical unit processes in a pulp mill. The burning process of black liquor is also quite sensitive to various external and internal disturbances. Proper, even control of the boiler is therefore of primary importance.

Through the Autorecovery installations, it has been shown that investment recoupment time is about one year. The main savings are achieved from: higher capacity and improved thermal efficiency, lower energy consumption (e.g. sootblowing steam), chemical savings and decreased emissions. The operation of the boiler is also easier and safer because of better overall process control, effective reporting and minimization of human errors. Furthermore, decreased maintenance and corrosion costs are also anticipated due to more even and stable operation.

The first Autorecovery control system was started in 1976. Today there are more than 10 Autorecovery systems running in Finland and abroad. Because of the encouraging experiences with the computer control of the recovery boiler, we believe that during the following 10 - 15 years almost all the pulp mills will have a computerized control system for their recovery boilers.

References

1. P. Uronen, E. Jutila, O. Pantsar, "A practical approach to the control of recovery boilers", IFAC seventh Triennial World Congress, Helsinki 1978, Preprints, Vol. 1.

2. E. Jutila, O. Pantsar, P. Uronen, "Computer control of a recovery boiler", Pulp and Paper Canada, 79(1978)4, pp T143 - T146.

3. O. Pantsar "Computer control for recovery boiler is succesful at Finnish mill", Pulp & Paper, Aug 1979.

4. E. Jutila, P. Uronen, N. Huovinen, H. Peltola, "Improved recovery boiler control system reduces energy costs, Pulp & Paper, July 1981.

5. P. Valkama, O. Pantsar, "Experiences on recovery boiler computer control in Finland", 1981 Int'l Cong. on Recovery of pulping Chemicals, Vancouver 1981. Preprints.

SAVINGS IN SOOTBLOWING OF RECOVERY BOILERS ACHIEVED BY TAMPELLA'S COMPUTER CONTROLLED SOOTBLOWING SYSTEM

by T.J. Ruohola, Manager R & D
Tampella Ltd, Boiler Division, Tampere, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

SAVINGS IN SOOTBLOWING OF RECOVERY BOILERS ACHIEVED BY TAMPELLA'S COMPUTER CONTROLLED SOOTBLOWING SYSTEM

T.J. Ruohola, Manager R & D
TAMPELLA LTD, Boiler Division, Tampere, Finland

Introduction

In pulp and paper industry the recovery boiler is one of the most sensitive devices when talking about mill availability. The boiler tends to get plugged because of the salt ash flying with the flue gas through the boiler. Rather heavy sootblowing is needed to keep the boiler open. Such sootblowing consumes much steam, 5...15 % of the steam production of the boiler. It is also difficult to know in which spot and when sootblowing is most needed because the operators have not enough time to carefully observe the boiler instrumentation and to do the complicated deductions necessary to perform the sootblowing right. So, by putting a computer constantly in charge of the boiler, with good instrumentation, remarkable savings can be achieved in steam consumption, up to 40 % compared to earlier figures. Also the reliability of the boiler increases and the operators get more information of the function of their boiler.

History

From the beginning of the spray type recovery boilers the steam sootblowing has been the dominant cleaning method. There have also been many attempts to carry out the salt removal from the surfaces in other, more economical ways, for example, vibrations, ultra and infrasound, or by adding different additives into the layers to make their removal easier. Also shot cleaning has been used in economisers of older boilers. Latest research work has shown that high pressure water sootblowing can be better than steam.

In most of today's sootblowing systems there are 26 (or 52, if they are on both sides of the boiler) rotating, retractable sootblowers (Fig. 1 & 2), which one by one clean different parts of the boiler.

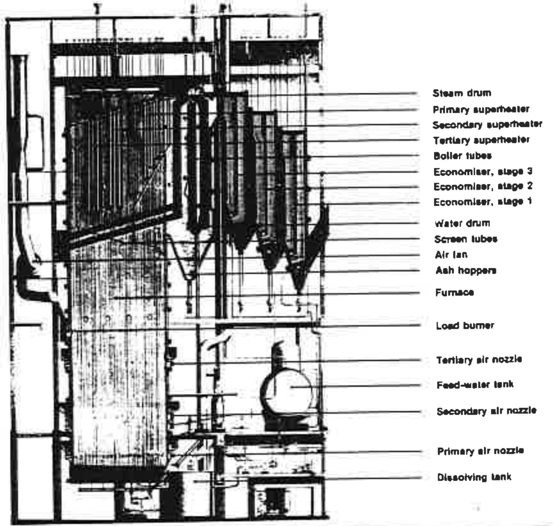


Fig. 1. Typical Tampella Recovery Boiler and the Arrangement of the Sootblowers.

Because of this great number of devices, they have been arranged to operate automatically by means of different automatic control systems.

The first, and also today much used method is a system where the sootblowers operate one after the other in fixed sequence, and each sootblower can be in the sequence only once. The operator can switch off the sootblowers from the sequence and thus weigh the amount of cleaning in different parts of the boiler. Electrically this method is based mostly on relay techniques. This system is rather much dependent on the operators, and because they are responsible for the availability of the boiler, they are eager to blow as much as possible, in fact all the time. Next step in this field is a system where different sequences can be freely programmed so that, for instance,

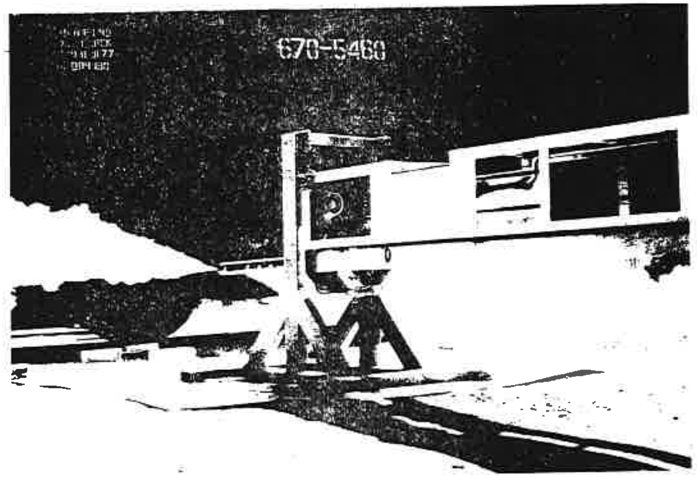


Fig. 2. A Steam Sootblower under Testing.

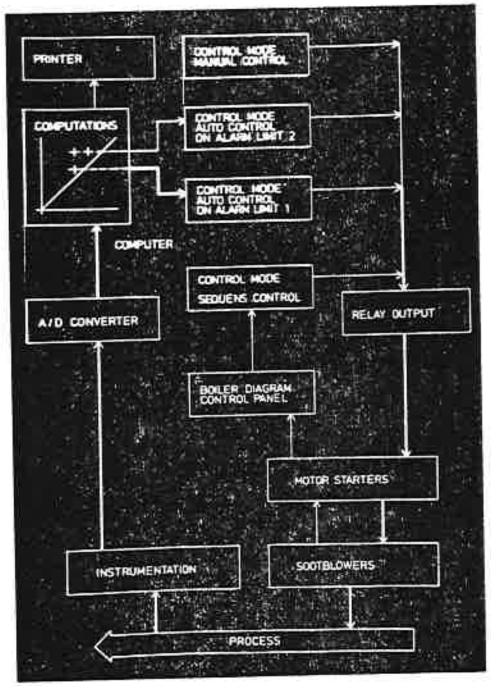


Fig. 3. Block Diagram of T.C.S.

sootblower No. 6 is 4 times in the program while blower 1 comes only once. The operators do not determine the sootblowing. There are different ready sequences for different operation conditions of the boiler, and the boiler manager can determine which sequence is used. This is usually arranged by means of cards or tapes or a drum where one can change the positions of the switches. Thus, this system is dependent on the boiler manager.

Tampella Computer Controlled Sootblowing System (T.C.S.)

To make the cleaning event dependent on the conditions of the boiler and to prevent the human subjective influence thereon, Tampella has developed an automatic sootblowing system where the system itself makes decisions of the actual cleanliness of the boiler and concentrates more sootblowing steam on spots where the situation is worst.

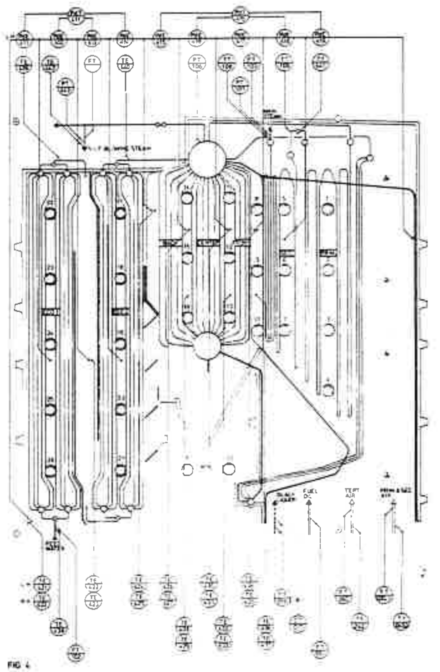


FIG 4

Fig. 4. Diagram of the Instruments which are Used in the Computerized Sootblowing System.

Fig. 5. The T.C.S. Computer Cubicle under Fabrication.

This is carried out by a mini-computer and some additional instrumentation in the boiler.
Fig. 3 illustrates the rough block diagram of the system consisting of:

- field instrumentation
- computer cubicle
- operation board on the panel
- printer

Fig. 4 shows the P & I diagram of the instrumentation. The boiler is divided into different parts over which pressure loss and temperature differences are measured. Also as input values for computing, general boiler data are taken to make necessary corrections according to boiler load or fuel quality.

Fig. 5 illustrates the computer cubicle. It is as any process computer with 32 k memory. The computer changes the measured values into friction coefficients and heat transfer conductances and compares them with normal values. Depending on deviations, the computer sends sootblowers into different parts of the boiler, more sootblowing into spots where the deviations are at the highest.

Fig. 6 shows the operation board on the panel through which the boiler operators can control the sootblowing without playing with the complicated computer programs. They can, for instance, manually add cleaning in different parts of the boiler.

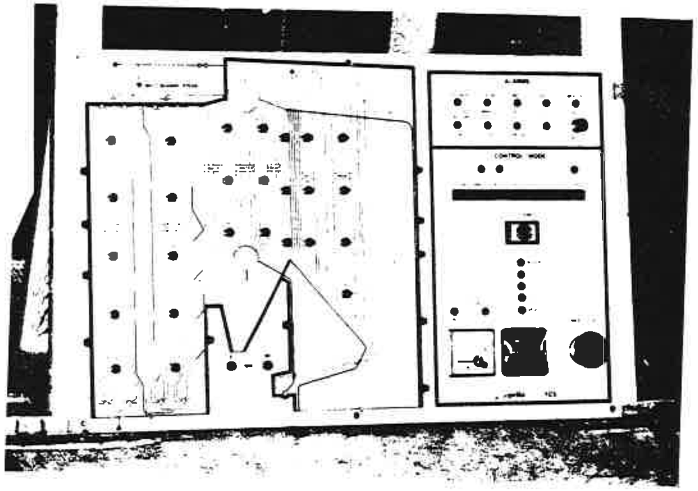


Fig. 6. Operation Board in the Panel.

The operators get information constantly of the situation in the boiler through the printer. Computer programs can also be changed through the printer.

Systems Delivered and Their Function

Tampella has made five T.C.S. units:

- United Paper Mill Ltd, Tervasaari, Finland, start-up 8/1976
- ASSI, Lövholmen Mill, Piteå, Sweden, start-up 11/1977
- NCB, Köpmanholmen Mill, Köpmanholmen, Sweden, start-up 4/1979
- International Paper Co, Ticonderoga, N.Y., USA, start-up 1/1982
- Svetogorsk, USSR, supplied 11/1981 but not yet started-up

All other applications are in Tampella Recovery Boilers except Ticonderoga, which is a B & W Boiler.

The first system delivered in Tervasaari was the prototype. The system was in operation for about 2 years. Due to some mistakes in hardware it was too difficult to keep in operation, and today the system does not work. Then the hardware was changed.

The T.C.S. in Piteå, Sweden has been in operation all the time from the start-up except for shorter shut-downs. The results have been satisfactory in saving of sootblowing steam as well as in boiler availability. The operators are so used to the T.C.S. that they had to relearn to operate the boiler without the T.C.S.

The second application in Sweden, NCB, also started promisingly, and the operation of sootblowing was satisfactory. But now, this summer, the whole mill will be shut down due to shortage of raw material and bad economic situation. Also in recent times, the effort in saving sootblowing steam has not been notably efficient.

The fourth application in Ticonderoga, USA, has now operated for half a year, and the results have reached those of ASSI, Sweden.

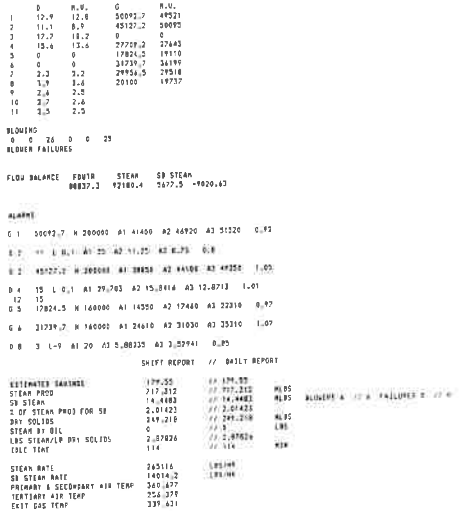
The fifth T.C.S. to USSR has not been started up yet.

It is evident that mills with a person who controls the system and weekly or daily checks it, have produced very good results, but at negligence, sooner or later something in the system goes wrong and the operators loose confidence and interest and the system does not work. We have also one problem; the computer which we use is not quite up-to-date, and in the next application we have planned to replace it.

Economical Results with the T.C.S.

In ASSI, Piteå, Sweden they have been able to operate the boiler with the T.C.S. so that the sootblowing steam consumption has been on the level of 7.5 t/h without plugs in the boiler. This is 4.22 % of the main steam production. In the beginning of the operation of the T.C.S.the figures were even lower, 5.3 t/h or 3 %. Earlier, before the start-up of the T.C.S., the figures were 11.5 t/h or 7 %. Hence, the saving has been 4 t/h.

During this first half year in Ticonderoga the savings have been 40 % in the consumption of the sootblowing, which in this case is 3.4 t/h (Fig. 7).



```
        D       M.V.    G         M.V.
  1     12.9    12.8    50092.7   49521
  2     11.1    8.9     45127.2   50095
  3     17.7    18.2    0         0
  4     15.6    13.6    27709.2   27643
  5     0       0       17824.5   19110
  6     0       0       31739.7   36199
  7     2.3     3.2     29956.5   29518
  8     1.9     3.6     20100     19737
  9     2.4     2.5
  10    2.7     2.6
  11    2.5     2.5

BLOWING
 0   0   26   0   0   25
BLOWER FAILURES

FLOW BALANCE   FDWTR     STEAM     SB STEAM
               88837.3   92180.4   5677.5   -9020.63

ALARMS

G 1   50092.7  H 200000  A1 41400  A2 46920  A3 51520   0.97

[illegible]   ** L 0.1  A1 25  A2 11.25  A3 8.75   0.8

G 2   45127.2  H 200000  A1 [illegible]  A2 [illegible]  A3 [illegible]   1.03

D 4   15  L 0.1  A1 29.703  A2 15.8416  A3 12.8713   1.01
 12   15
G 5   17824.5  H 160000  A1 14550  A2 17460  A3 22310   0.97

G 6   31739.7  H 160000  A1 24610  A2 31030  A3 35310   1.07

D 8   3  L-9  A1 20  A3 5.88235  A3 3.52941   0.85
                         SHIFT REPORT   //  DAILY REPORT

ESTIMATED SAVINGS              179.55     // 179.55
STEAM PROD                     717.312    // 717.312    MLBS
SB STEAM                       14.4483    // 14.4483    MLBS   BLOWERS A [illegible] FAILURES [illegible]
% OF STEAM PROD FOR SB         2.01423    // 2.01423
DRY SOLIDS                     249.218    // 249.218    MLBS
STEAM BY OIL                   0          // 0          LBS
LBS STEAM/LB DRY SOLIDS        2.87826    // 2.87826
IDLE TIME                      114        // 114        MIN

STEAM RATE                     265116     LBS/HR
SB STEAM RATE                  14014.2    LBS/HR
PRIMARY & SECONDARY AIR TEMP   360.677
TERTIARY AIR TEMP              256.379
EXIT GAS TEMP                  339.631
```

Fig. 7. Information Achieved through the Printer from the Boiler and from the Sootblowing.

In cases, where the system has been well cared for, the savings have been 3.8 t/h in average. If no electricity is taken from the steam before it goes to sootblowing and the mill uses oil to produce the top amount of steam, we can calculate that the value of the steam is USD 13/ton. Total saving per year is:

3.8 t/h x 8000 h/year x USD 13/t = USD 395,200/year
=================

Other possible savings have not been carefully measured, but, for instance, the sootblower needs less maintenance, the efficiency of the boiler is slightly higher and the flue gas fans need less power.
On the cost side, the system needs the attention of the person in charge, but on the other hand, the boiler operators need not observe the sootblowing so carefully.

Summary

In cases where interest has been placed in saving sootblowing steam, the pay-back time of the T.C.S. investment has been 0.5...1.0 years. Also in boilers where the results are good, difficulties have occured earlier in sootblowing, and operators have known that they blow too much but failed to locate the problem.

EXPERIENCES OF TWO YEARS OF WATER SOOTBLOWING IN KEMI

by

J. Alajärvi, Superintendent, KEMI Oy, Kemi, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

EXPERIENCES OF TWO YEARS OF WATER SOOTBLOWING IN KEMI

J. Alajärvi, Superintendent
KEMI Oy, Kemi, Finland

1. Abstract

The sootblowing of the recovery boiler has been of great interest to many because of its high energy consumption. In general attempts have been made to reduce the energy consumption and to improve the sootblowing by using different control systems. One way of improving the sootblowing efficiency on the superheater is water sootblowing.
This paper presents the results of water sootblowing on the recovery boiler at Kemi Oy. The experiments were carried out in order to find out the sootblowing efficiency and the corrosion speed of the superheater tubes.

2. Introduction

The first water sootblowing experiment on the superheater of the recovery boiler was conducted in Kemi in close co-operation with the Finnish Recovery Boiler Committee in 1976. During the experiment (appr. 1 month) was examined the efficiency of water sootblowing compared with steam sootblowing. The positive results of the experiment lead to a further test in 1980. Besides the sootblowing efficiency the corrosion speed of the different materials used on the superheater during the water sootblowing was examined.

3. Equipment

The water sootblowing experiments were conducted in Kemi Oy:s (Kemi, Finland) small recovery boiler, the capacity of which is appr. 350 tons dry solids per day. There are 15 sootblowers in the boiler and those 4 on the superheater area have been converted into water sootblowers (FIGURE 1):

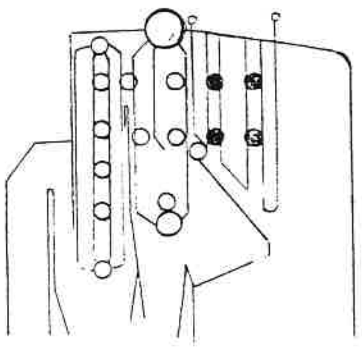


FIGURE 1. Location of sootblowers

The sootblowers on the superheater (Tampella) can be used both for steam and water sootblowing. The water sootblowing system consists of pressure pump, pressure measurements with the upper limit alarms, safety valve and a locking system for the upper limit of the water amount (FIGURE 2). The flushing air for the blowers is taken from the tertiary air channel.

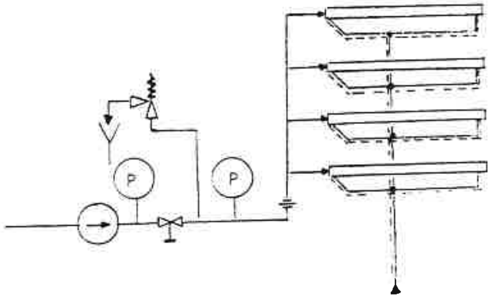


FIGURE 2. Water sootblowing system

The operation parameters of the equipment are:

- angle of nozzle declivity 10°
- nozzle diameter Ø 3,7 mm
- nozzle operating time appr. 7 min
- jet pressure 16 - 17 bar
- water amount 0,9 - 1,0 l/s

Besides some smaller difficulties at the beginning we have had no problems with the equipment. It has caused no danger moments, either.

4. Sootblowing efficiency

At the beginning of the experiment it happened that the operation parameters were chosen wrong and this caused some trouble. After the nozzle angles were changed, bigger nozzles were taken into use and the operating period of the sootblower was prolonged the desired sootblowing efficiency was reached. At the same time it was possible to drop the number of sootblowings from four to two per day (on the superheater area). When using steam sootblowing (4 times per day) a temperature of appr. 397°C was reached to the developed steam ($p \sim 56$ bar). After having changed the operation parameters it has been possible to reach an approximate temperature of 414°C with the water sootblowing (2 times per day)(FIGURE 3). The water amount required on the superheater is appr. 10 t/d lower than the required amount of steam. During the water sootblowing the temperature of the heater goes up 25 - 30°C (FIGURE 4).

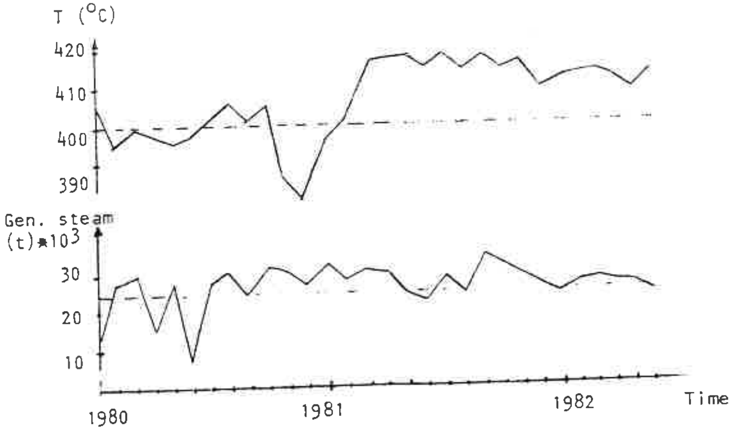


FIGURE 3. Temperature of steam produced during water sootblowing

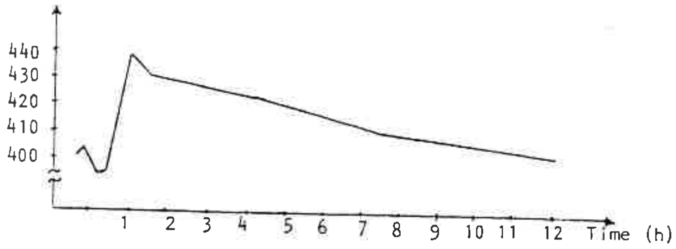


FIGURE 4. Rise of temperature of steam produced during water sootblowing

According to visual observations the surfaces of the superheater tubes are totally clean in the area, where the water sootblowing was effected, but the "back side" of the tubes did not get properly clean.

5. Corrosion test

The second purpose of the experiment was to find out the effect of the water sootblowing on the corrosion speed of the superheater tubes. To carry out this test 8 sample tubes were installed on the heater area, near to the water sootblowers (FIGURE 5):

- 4 pcs Ø 63.5 * 6.3, 13 Cr Mo 44
- 2 pcs Ø 63.5 * 6.3, 15 Mo 3
- 2 pcs Ø 63.5 * 6.3, SIS 2343

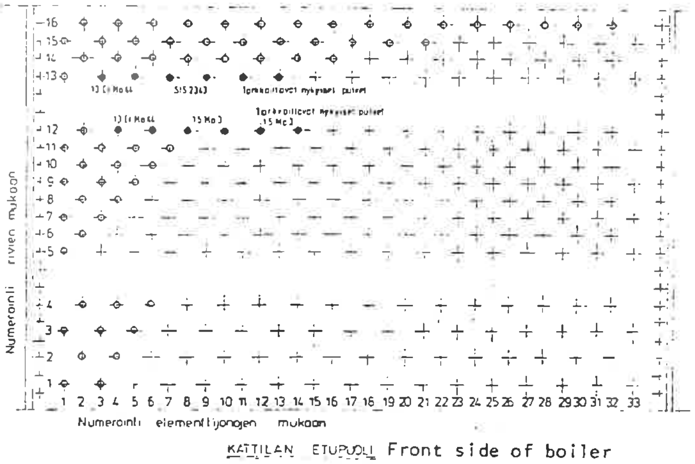


FIGURE 5. Location of sample tubes on superheater area

The sample tubes and four old tubes were controlled three times during the test period:

- visual checking
- wall thickness measurement (TABLE 1)
- cracking test with Magnaflux-method (Parker Contour Probe DA-200S)

At the third control small pores were observed in the lower welding seam of tube 4/12 and in the upper welding seam of tube 10/12. No damage was observed either at the visual checkings or in the thickness measurements.

Tube	Check-ups			
	1 (mm)	2 (mm)	3 (mm)	4 (mm)
4/12	6,21	6,06	6,34	6,33
6/12	6,34	6,13	6,33	6,25
8/12	6,17	6,05	6,30	6,40
10/12	6,43	5,95	6,19	6,34
12/12	6,14	6,14	6,27	6,26
14/12	6,22	6,09	6,34	6,35
3/13	6,06	5,90	6,79	6,13
5/13	6,10	6,03	6,85	6,20
7/13	7,00	6,89	7,45	6,43
9/13	7,02	7,02	7,61	7,16
11/13	6,10	5,92	6,78	6,12
13/13	6,05	5,95	6,78	6,03

TABLE 1. Wall thickness measurements

Of the sample tubes 3 were removed for laboratory tests:

- tube 4/12, 13 Cr Mo 44
- tube 7/13, SIS 2343
- tube 10/12, 15 Mo 3

The results of the tests are not yet available.

During the experiment period Oy Keskuslaboratorio carried out two tests with the corrosion sond. The materials of the sond were carbon steel (St. 45.8) and corrosion-resisting steel (SIS 2333). The result of the test was following:

- no crackings were observed in the sample pieces taken from the sond
- at the highest temperatures it is possible that the water sootblowing accelarates corrosion of carbon steel
- at corrosion-resisting steel the corrosion speed has remained constant as function of temperature
- the surface temperature of the clean sond dropped 71°C during the water sootblowing
    - change of temperature after sond had become dirty was much smaller

6. Benefits obtained

Of the benefits reached with the water sootblowing following are unambiguous:

- the water amount is appr. 10 t/d smaller than the steam amount on the superheater
- increase of power development caused by increased superheater temperature (17°C)

To evaluate the thermal efficiency is relatively difficult.

Savings calculation:

- energy saving due to lower energy consumption during water sootblowing		200.000 mk
- increase in power development		50.000 mk
- growth of thermal efficiency		100.000 mk
- annual saving	appr.	350.000 mk

7. Summary

The sootblowing was functioning good. No risk moments were observed in the boiler during the experiment.

The efficiency of water sootblowing was greater than that of steam sootblowing. The obtained annual saving amounted to 250.000 - 350.000 mk.

Water sootblowing caused no abnormal corrosion on the materials used (carbon steel ?). The laboratory tests of the sample pieces are not yet ready.

OPERATING EXPERIENCE AND OTHER CRITERIA IN RECOVERY BOILER CONTROL SYSTEM APPLICATIONS

by

H. Tarvainen and T. Roos, EKONO Oy, Helsinki, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

BLRBS 1982

OPERATING EXPERIENCE AND OTHER CRITERIA IN RECOVERY BOILER CONTROL SYSTEM APPLICATIONS

Heikki Tarvainen and Tom Roos
EKONO Oy
Helsinki, Finland

1. Abstract

The critical nature of recovery boiler in liquor circulation and difficulties in burning control have necessitated extensive research of black liquor burning and recovery operations. Following the process research, control system development projects led to installation of control systems that have been operational for years.

In many cases the installation of the control system took place in conjunction with repairing or rebuilding the boiler. The results of the project must therefore be judged in its entirity.

Generally speaking the pay-back time has been between 0.5 to 2 years. Most of the benefits resulted from increased dry solids throughput. An additional advantage is decreased steam consumption for sooting. Further, design criterias for liquor spraying and air distribution were developed.

Computer systems have been effective in completing process studies and in the evaluation of control strategy. It has been established that computer systems lead to good operating results. This is true even in cases where difficulties with normal instrumentation and automation have been encountered.

2. Introduction

The two original boiler types were Combustion Engineering (CE) and Babcock and Willcox (BW). Mixed types are currently in operation having characteristics derived from both the above original models.

Although the chemical reactions and the heat balance are basically the same in each type of boiler, the liquor burning characteristics vary greatly with individual boilers.

Regardless of differences in method of burning, the basic principles of burning control are the same with all boilers.

3. Black Liquor Burning

3.1 Objectives of black liquor burning are:

1) To achieve a high reduction of Na_2SO_4 to Na_2S
2) To recover the heat of liquor dry solids most effectively in high pressure steam
3) To minimize the release of gas and solid pollutants into the atmosphere.

The above objectives must be achieved while at the same time preventing boiler corrosion and maintaining safety. This must be done despite the fact that there is generally a need to burn more dry solids than the boilers original planning stipulated.

For effective regeneration of cooking chemicals a high temperature and a reducing atmosphere is required. This is most easily achieved if most of the liquor burning takes place in and on the charbed or in gases immediately above the bed.

In order to avoid emissions and to enhance steam generation sodium should be sufficiently vaporized to react with sulphur gases. This action decreases fouling of the boiler. Further, it established an atmosphere less favourable for corrosion.

Maximum temperature is found immediately above the charbed. At this location the liquor should be burned. High temperature there is also necessary for chemical regeneration. An additional advantage of burning the liquor in the charbed region will be the cooling of gases in the upper region. This will reduce the risk of sticky deposits on the superheater tubes. Decreased fouling of the tubes permits greater heat economy and improved solids throughput.

3.2 Description of controllable method of liquor burning

3.2.1 Liquor delivery

The liquor is sprayed using stationary flash plate nozzles. The correct droplet size is achieved by proper dimensioning of nozzle diameter along with determining suitable nozzle angle and spraying pressure. Liquor droplets generated in this manner will be dry upon reaching the charbed region.

3.2.2 Air delivery

Two independent air supplies, a primary and a secondary, are required for the charbed.

The primary air is introduced uniformly with the boiler a short distance above the boiler floor. Its pressure is such that it only penetrates a short distance into the furnace.

The secondary air is applied at a height approximately 1.5 m above the level of the primary air. Its pressure which is significantly higher than the primary air pressure is designed to force air into the center of the furnace at the charbed top.

The great majority of the air in the furnace, at least 70 %, is comprised of the combined primary and secondary air.

All primary and secondary air ports are equipped with individual jets which have variable area adjustment control. In this way the velocities and volume flows of individual streams of air entering the furnace can be adjusted independently.

3.2.3 Boiler Symmetry

Symmetry of both the black liquor sprying system and the air delivery system is a design requirement. Locating secondary air ports or all four walls seems favourable. Further, air ports placed near corner must be located in such a way that the corner will not be cooled.

3.2.4 Charbed height control

It is of major importance to maintain a stable charbed. Variations in charbed height alter the liquor burning rate. The dry solids / total air ratio is also usually a variable of char bed height. Is is unlikely that a constant burning rate and stable charbed can be controlled only by the droplets and spraying. Introducing low secondary air approx. 1.5 m above the primary register is an effective way to control the bed. Moreover, the burning becomes almost self-controlling. Further, the use of low secondary air reduces the requirement for primary air, which in turn favours the degree of reduction to be high.

4. Control of Black Liquor Burning

4.1 Controllability

Excepting liquor properties, the type of boiler and its geometry are decisive factors in recovery boiler controlability. This has been determined by operating experience with recovery boilers and their control systems.

Although it is possible to burn liquor in every known type of boiler, the overriding advantages of the two air register design is the stabilizing of the bed height, which is the key factor for enhancing black liquor burning.

General furnace symmetry is a further aid to controllability. In this way the need of separate control action for different parts of the furnace is avoided. Also the possibility of setting tight and optimal control targets is improved.

4.2 Characteristics of Recovery Boiler Control

The all important task in recovery boiler control is to maintain a stable and unchanged charbed. This is essential to maintain a balance between dry solids feed and air supply.

Disturbances will be due to variations in liquor properties. These include elementary analysis, dry solids content, heat value and viscosity. Other disturbances result from clogging of liquor nozzle or air ports as well as random disturbances in the furnace itself.

It is very difficult to determine which variable originally causes deviation from target boiler output and subject it to control action. This is due to the fact that furnace reactions are so numerous and every input influence black liquor burning. Further, these influences are not always predictive. Successfully every boiler control must, therefore, have a feedforward nature. The primary feedforward function is to determine and supply the total air needed to burn the dry solids fed to the furnace.

Within a certain region in recovery boiler furnace the above mentioned variables have a linear or near linear relationship. In other locations relationships are unpredictive and normally increasing factors change to decreasing. Most of the variables by recovery furnaces have their safe operating region where variations can be compensated and controlled.

The recovery boiler control strategy could be described as follows:

1) Find a safe and controllable operating region for your individual boiler and black liquor.
2) Maintain the operation in that region using all possible feed-forward compensations and monitoring information.
3) Perform a continuing process identification and study to verify the parameters of liquor burning and boiler fouling.
4) Prevent as far as possible all changes in boiler load and operating mode.

5. Control Systems Application Results

Computerized recovery boiler control operations were firs realized with the 70's. By 1975-76 the second generation, or commercial recovery boiler control systems, were operational. Currently there are 30 recovery boilers equipped with a computerized or digital control system.

In every case reported the results with recovery boiler control systems have been successful.

The most important benefits have been decreased boiler fouling and reduced steam consumption for sooting. Because of less fouling and steady and smooth operation the solids throughput has also increased. Further, reduced excess air and decrease in flue gas temperature have improved thermal efficiencies of the boilers.

Improvement in chemical regeneration has resulted from more efficient reduction. There has also been a decrease in the amount of emissions released. H_2S and SO_2 emissions can be nearly eliminated when the sulphur level of the black liquor is within normal range.

The projects in which a boiler having originally only one air register on the bed level was rebuilt and equipped with a computer control system increase in throughput and reduction efficiency was in the magnitude of 3 to 5 times greater than boilers already having low secondary air. The rebuilding included installation of low secondary air and plate type nozzles.

The study period required for implementation of a recovery boiler control project also results in increased understanding of the recovery boiler operation by the operating personnel.

In the case of reliable, smooth operating control system, elimination of the human factors associated with change of operators 3 times a day further stabilizes the performance.

INVESTIGATION OF FIRESIDE DEPOSITION AND CORROSION IN SULPHATE AND SODIUM SULPHITE RECOVERY BOILERS

M. Hupa, Åbo Akademi, Turku, Finland
R. Backman, Åbo Akademi, Turku, Finland
P. Hyöty, Oy Tampella Ab, Tampere, Finland

1. Introduction

This paper summarizes some recent results of an extensive research program, which deals with fireside problems in recovery boilers. In the program special attention has been paid to differences in the behaviour of the common sulphate liquors compared with sodium sulphite liquors. Although sulphate and sodium sulphite liquors are burned in same-type of recovery boilers, the two liquors differ from each other quite considerably. The chemical constituents, both organic and inorganic, are very different in the two liquors. Also some of the physical properties are different.

Consequently, many practical differences may be expected both in the lower part of the furnace and in the flue gases of the boilers burning these two types of liquors.

The discussion in this paper is divided into two parts:

- the formation and importance of acidic sulphates in the fly ash and deposits,
- the superheater deposit problems and carry over of liquor droplets from the lower part of the furnace.

2. Experimental

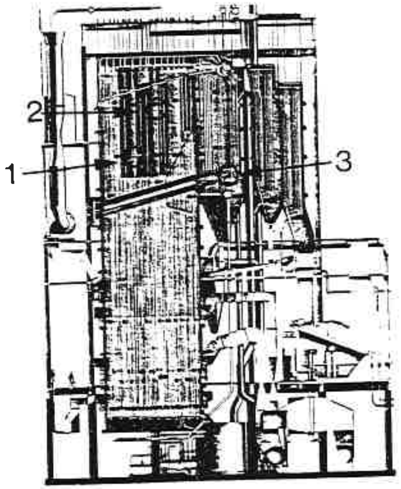
The present work is mainly based on deposition and corrosion investigations in four sulphate and two sulphite boilers. In each boiler short-term deposit and corrosion samples were collected by means of air-cooled probes /1/. The probes, consisting of two co-axial tubes, were some 2 m long and had a diameter of about 40 mm. The cooling air entered the inner tube and left through the intermediate space between the tubes. A detachable sampling ring was screwed onto the probe some 120 mm from the end of the tube. The temperature of the sampling ring surface was followed by [illegible] thermocouples and automatically controlled by means of an electric valve connected to the input tube of the cooling air. The sample times were varied between 15 min and some 20 hours. After exposure in the boiler the sampling ring was removed from the probe and examined by different techniques including:

- photography
- scanning electrone microscopy (SEM)
- energy dispersive X-ray micro analysis (EDXA)
- chemical analysis of the aqueous solution of the ring deposit.

Samples were taken both from the superheater region of the boilers and immediately after boiler bank tubes (Fig. 1).

Figure 1. Sample areas in the investigated boilers.

1. Superheater lower level
2. Superheater higher level
3. After boiler bank tubes



3. Acidic sulphates

3.1 S/Na_2 in flue gases

One of the most essential differences between the sulphate and sulphite liquors is, naturally, the "sulphidity" of the liquor, here defined as the molar ratio S/Na_2. This ratio is in sulphate liquors 0,2...0,5 and in sulphite liquors 0,9...1,5, sometimes even higher (Table 1). This leads to a still greater difference in the S/Na_2 ratio in the flue gases. In sulphite boilers the SO_x-content is several thousands of ppm, which means a considerable stoichiometric excess of sulphur compared to sodium, S/Na_2 2...12. In sulphate boilers the SO_x concentration in the flue gases seldom exceeds a few hundred ppm and, consequently, there is often only a slight, if any, excess of sulphur, S/Na_2 being around unity or less. This leads to a very different chemistry in the flue gases and fly ash of the two systems.

Table 1. The molar ratio S/Na_2 in liquor, smelt and flue gases in sulphate and sulphite boilers.

	LIQUOR S/Na_2 mole/mole	SMELT S/Na_2 mole/mole	FLUE GASES SO_x ppm (vol)	*) Na_2SO_4 g/nm^3	S/Na_2 mole/mole
SULPHATE	0,2...0,5	0,2...0,3	50...500	6...25	0,9...1,8
SULPHITE	0,9...1,5	0,5...0,7	2000...10000	5...15	2...12

*) gram per cubic meter dry flue gas at 0 °C and 1 atm.

The principal chemical reactions between sulphur and sodium in the oxidizing part of the furnace and in the flue gases in the two types of boilers are summarized in the flow sheets in figure 2 /2/. The most important compounds in the flue gases are presented as a function of the flue gas temperature. The reactions leading to the compounds indicated in the flow sheets are discussed in more detail in ref. 2, 3 and 4.

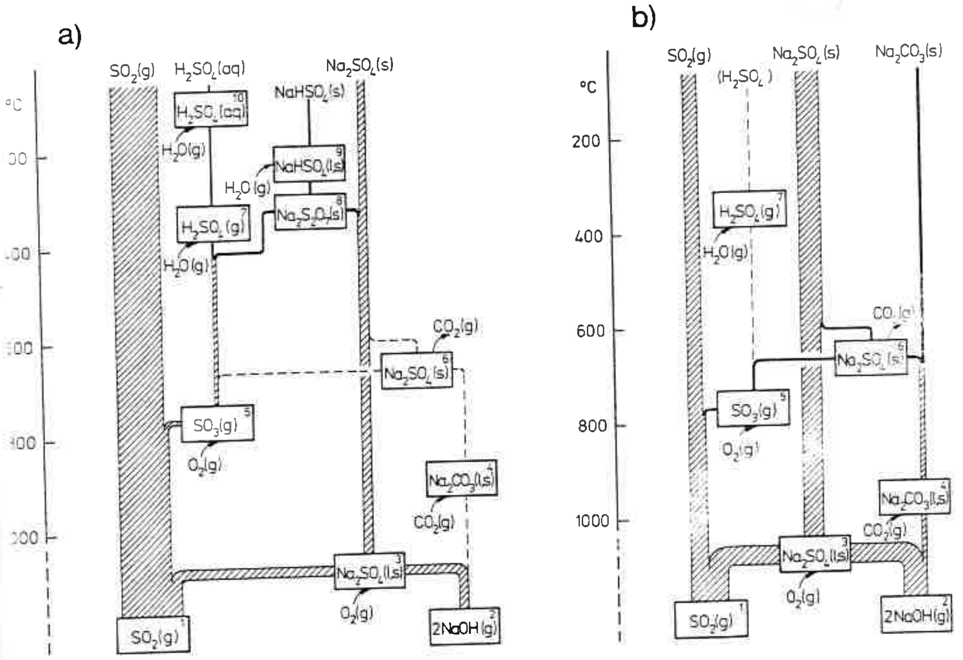


Figure 2. The most important reactions of sodium and sulphur in recovery boilers. a) S/Na$_2$ = 6 mole/mole (sulphite), b) S/Na$_2$ = 1,5 mole/mole (sulphate).

Due to the large excess of SO$_2$, the sodium compounds, mostly hydroxide and carbonate, are quantitatively converted to Na$_2$SO$_4$ already at an early stage in a sulphite boiler (Reaction square 3 in fig. 2a). The small amount of SO$_3$ which may be formed in the flue gases later on (square 5) may consequently react with the Na$_2$SO$_4$ forming acidic sulphates, pyrosulphate, Na$_2$S$_2$O$_7$, or bisulphate, NaHSO$_4$ (squares 8 and 9).

The same does not normally happen in sulphate boilers (Fig 2b). There is usually enough sodium carbonate present to neutralize the SO$_3$ at an early stage (square 6 in fig. 2b), thus preventing the formation of acidic sulphates.

3.2 Thermodynamic stability of acidic sulphates

Figure 3 shows the best up-to-date p_{SO_3} - T -phase diagram of the system Na$_2$SO$_4$-H$_2$O-SO$_3$. The diagram is for the sake of simplicity constructed assuming no mutual solubility of the phases, although some phases are partially soluble in each other. The thermodynamic values are taken from ref. 5, 6 and 7. Although there is still some doubt concerning the accuracy of the thermodynamic values, the diagram may well be used to explain some practical observations.

Acidic sulphates are stable when the SO$_3$ (or more correctly SO$_3$ + H$_2$SO$_4$) concentration exceeds the value indicated by the border line to Na$_2$SO$_4$. Obviously, the higher the temperature, the higher SO$_3$ (or SO$_3$ + H$_2$SO$_4$) concentration is needed to stabilize the acidic sulphates. Thus, the corrosive liquid pyrosulphate (mp. 402 °C), which is sometimes quoted to cause corrosion in oil fired boilers /8, 9, 10/, already requires a very high SO$_3$ + H$_2$SO$_4$ concentration in a recovery boiler atmosphere, around 5000 ppm. Consequently, liquid sodium pyrosulphate is hardly conceivable in recovery boilers. Theoretically this high SO$_3$ + H$_2$SO$_4$ concentration could be reached in a sulphite boiler with total SO$_x$ > 5000 ppm inside the pores of a thick deposit, where the complete conversion of SO$_2$ to SO$_3$ is possible due to the long residence time. Also here, however, the presence of the liquid pyrosulphate would be restricted to a very narrow temperature interval, from the melting point, 402 °C, to some 450 °C, at which temperature the required SO$_3$ + H$_2$SO$_4$ concentration already exceeds 10000 ppm, a value higher than the total SO$_x$ concentration in any practical system.

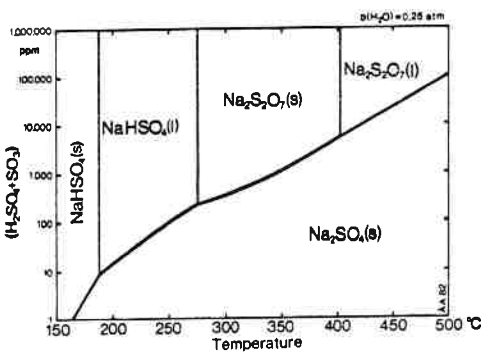


Figure 3. Stability diagram for the system Na$_2$SO$_4$-SO$_3$-H$_2$O. Total pressure 1 atm. Partial pressure of water 0,25 atm.

The well known, rapid plugging of economizers and the corrosion of boiler bank tubes /11,12/, are probably due to the presence of molten sodium bisulphate, $NaHSO_4$(l). This may form at, say 260 °C, if the SO_3 + H_2SO_4 concentration in the flue gases exceeds some 100 ppm. This, again, is possible in both sulphite and sulphate boilers with a high S/Na_2 ratio in the flue gases, if the catalytic SO_3-formation (Cf. fig. 2, square 5) is favoured. The most important practical variable affecting the SO_3-formation and thus also the formation of bisulphate, is the excess of oxygen in the flue gases /13,14/.

The best indication for the existence of acidic sulphates in the fly ash is the "pH of the fly ash", i.e. the pH of a, say 5 %, aqueous solution of the fly ash. If no other acidic compounds are present, one can calculate that a fly ash with pH = 3,0 contains 2,4 % $NaHSO_4$ and with pH = 2,0 already some 24 % $NaHSO_4$ /2/. A practical "critical" value with respect to plugging of economizers has been found to be around pH < 3,0 /2,15/.

3.3 Corrosion probe test

The short term corrosion probe tests seem to confirm the above discussion. Figure 4 shows the amount of dissolved iron from the corrosion probe rings plotted as a function of the sampling ring surface temperature after a 15 min. exposure in boilers with different S/Na_2 in the liquor. The samples were all taken from the boiler bank area according to fig. 1. The flue gas temperature at this place varied between 400 and 450 °C.

Table 2 shows some examples of the chemical composition of the aqueous solution of the corrosion probe deposits and fig. 5 shows some typical SEM images of the corrosion probe surface after the exposure.

It may clearly be seen, that the worst corrosion is faced in high sulphidity sulphite systems with high O_2 in the flue gases. However, in all cases the corrosion rate could be

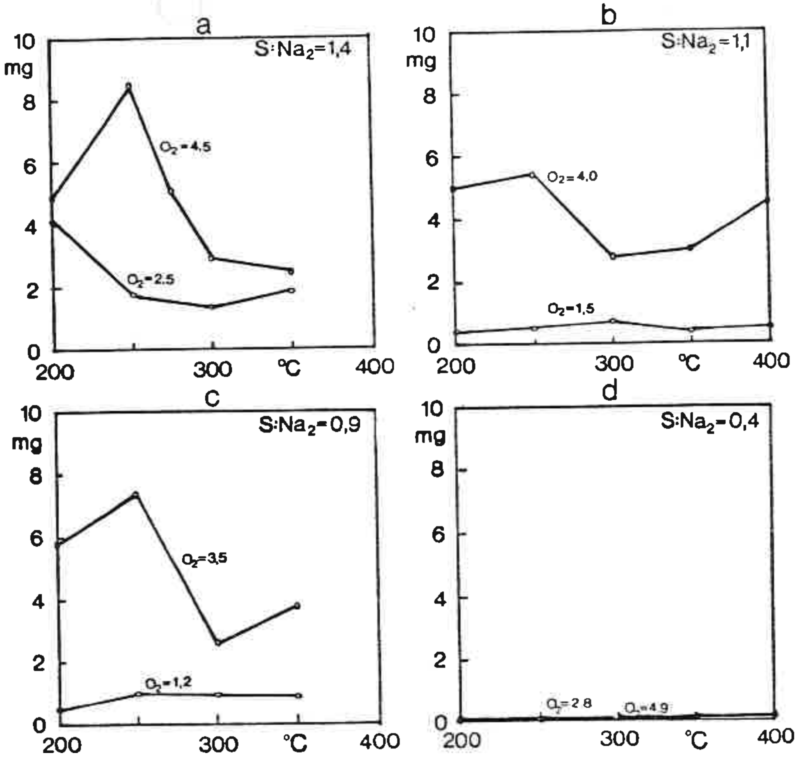


Figure 4. Results from the corrosion probe tests. The x-axis represents the sampling ring surface temperature, the y-axis the amount of dissolved iron oxide (Fe_2O_3) in mg. The sampling time was 15 min. in the boiler bank area. The O_2-values are percent excess oxygen in dry flue gases. The S/Na_2-ratio 1,4 was simulated by sulphur addition in a NSSC-boiler.

significantly lowered by running the boiler with an excess O_2 of less than ca. 2 %.

An interesting feature in all the corrosion curves with the high O_2 is the sudden drop of the corrosion rate between the temperature 250 °C and 300 °C. This could be explained by the decomposition of the corrosive, liquid sodium bisulphate to a considerably less corrosive, solid pyrosulphate at around 260...280 °C (Cf. fig. 3). Consequently, boiler pressures giving water temperatures higher than some 280 °C are obviously less sensitive to bisulphate corrosion problems in water tubes (boiler bank).

Table 2. The chemical composition of some corrosion probe samples from the boiler bank given as weight percent oxide of total sample weight.

	SULPHITE		SULPHATE	
O_2 (%)	1,5	3,5	2,8	4,9
Sample weight (mg)	89,5	26,2	58,7	73,7
pH (*	5,5	4,5	10,1	9,6
Composition				
Na_2O (weight-%)	42,8	38,1	41,6	48,4
K_2O	3,7	6,0	3,1	2,6
CaO	0,2	0,7	0,1	0,1
Fe_2O_3	0,9	10,7	0,1	0,1
SO_3	62,0	61,7	37,1	42,2
CO_3	-	-	20,2	12,8
Cl	0,8	1,4	2,2	1,7
	110,4	118,6	104,4	112,9

*) pH of the solution when the sample was dissolved in 50 ml water.

The corrosion rate in the sulphate boiler (Fig. 4d) is typically an order of magnitude lower, indicating the total lack of acidic sulphates.

Long term experience from sulphite boilers correlates very well with the presented short term corrosion test results /15/.

4. Superheater deposition and carry over

4.1 Deposition probe samples

Figure 6a shows a series of photographs of the sampling probe exposed to the flue gases in the lower part of the superheaters of a sulphate boiler (sampling point acc. to fig. 1). The sampling times were 15 min., 1,5 h and 3 h. In this boiler the deposit formation was very rapid and caused problems

due to insufficient super heating and finally also due to an untolerable flow resistance for the flue gases in the superheater region. Very similar deposits were also collected from the corresponding place in a sulphite boiler (Fig. 6b).

The probe samples show clearly the two types of fly ash constituents in the boiler atmosphere, recently also reported by Reeve, Tran and Barham /16/ (Cf. also fig. 5). The white powder represents condensed Na_2SO_4 originating from volatile sodium from the bed. The reddish, thick deposit is clearly a result of inertial impaction of black liquor droplet residues carried over with the flue gases from the burner level. The condensed white powder was almost pure Na_2SO_4, while the carry-over type, thick deposit contained a large amount of Na_2CO_3 and also some Na_2S (Table 3). The presence of some other reduced forms of sulphur may also be suspected due to the bright colours of the deposits. Thus it is obvious that the carry-over particles have been partially unburned when hitting the probe surface. The amount of other compounds in the deposits, like those of K, Cl or Ca, was always small in the six investigated boilers and, contrary to the situation in some closed cycle mills /16/, these compounds hardly have any significant influence on the deposit formation.

Table 3. The chemical composition of deposition probe samples from the lower part of the superheaters. Sample time 3 h. Weight percent of total sample weight.

	SULPHITE	SULPHATE
Na (weight-%)	40,0	35,6
K	2,4	1,4
$SO_4^=$	35,8	35,6
$S^=$	1,3	0,2
$CO_3^=$	25,9	22,0
Cl^-	1,1	0,8
	106,5	95,6

Na_2SO_4 and Na_2CO_3 form a solid solution with a lowest solidus temperature of 820 °C, above which the mixture is partially molten. With Na_2S as the third component the lowest solidus temperature drops to some 730 °C /16/. The presence of other reduced sulfur components, like disulphide, would still lower the temperature where the molten phase appears.

Obviously, the lower the flue gas temperature when entering the superheaters, the less molten phase in the deposit and the better the situation. Consequently, in colder parts of the superheaters (< 700 °C) the carry-over particles do not any more stick to the surfaces (Fig. 6c).

High flue gas temperatures in the superheaters worsen significantly the deposit problems. Especially an uneven distribution of the flue gas flow in the furnace may locally cause some very hot "spots" in the superheaters.

An other way to improve the situation is to suppress the amount of carry over by proper air distribution and burner adjustment (Fig. 6d).

4.2 Burning behaviour

Figure 7 show the typical appearance of a single droplet of both sulphate and sulphite liquor burning in a laboratory furnace. The atmosphere was pure air and the furnace temperature in the referred experiments was 700 °C, but very similar results were also obtained at higher temperatures.

Both liquors behave in a fairly similar manner during the drying period. On the other hand there is a dramatic difference between the two liquors during the escape and burning of the volatiles. The sulphate liquor droplet swells several hundred percent, while the sulphite liquor droplet hardly shows any swelling at all during this stage.

The considerable swelling of the sulphate droplet gives a large, porous carbon residue, which due to the large surface area burns more rapidly than the sulphite droplet.

The consequences of the different burning behaviour for instance to the type and amount of carry-over particles and to the optimal design of the lower part of the furnace (burners, air supply) are under consideration.

5. References

1. Hupa, M., Eriksson, B-E., Klingstedt, G., Paperi ja Puu - Papper och Trä 60(1978)11.
2. Hupa, M., Paperi ja Puu - Papper och Trä 62(1980)9.
3. Hupa, M., Paperi ja Puu - Papper och Trä 62(1980)6-7.
4. Hupa, M., Paperi ja Puu - Papper och Trä 62(1980)1.
5. Ingraham, T. R., Hotz, M. C. B., Can. Met. Quart. 7(1968)3.
6. Flood, H., Förland, T., Acta Chem. Scand. 1(1947)781.
7. Barin, I., Knacke, O., Thermochemical properties of inorganic substances, Springer Verlag, Berlin 1973.
8. De Santis, R. , Corrosion Prevention & Control, 20(1973)6.
9. Bryers, R., ed., Ash Deposits and Corrosion due to Impurities in Combustions Gases, Hemisphere, Washington/ London 1978.
10. Coats, A. W., Dear, D. J. A.,Penfold, J., J. Inst. Fuel 41(1968)129.
11. Gerdin, S., Jönson, S-E., Moberg, O., in "Proceedings on the Symposium on Recovery of Pulping Chemicals", IUPAC-EUCEPA, Helsinki 1960.
12. Reid, W. T., External Corrosion and Deposits, Boilers and Gas Turbines, American Elsevier, New York 1971.
13. Leitham, J., Engen, R., Folsom, M., Pulliam, T., Tappi 61(1978)37.
14. Hyöty, P., Pulp Paper Mag. Canada 80(1979)115.
15. Kuukkanen, K., Nikkanen, S., Hyöty, P., International Sulphite Pulping Conference 1982.
16. Tran, H., Ph.D. thesis, University of Toronto 1982.

APPENDIX. Figures [illegible] and 7.

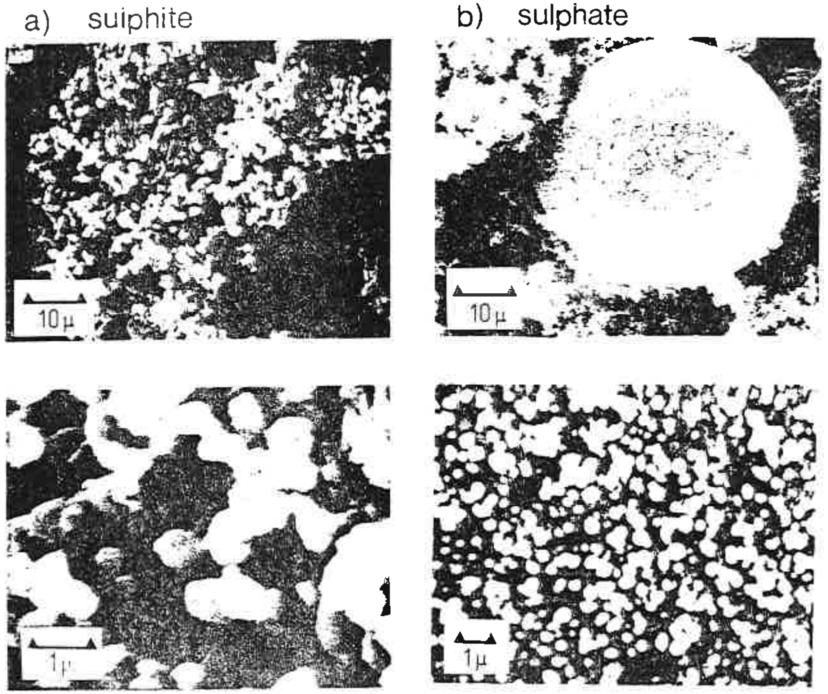
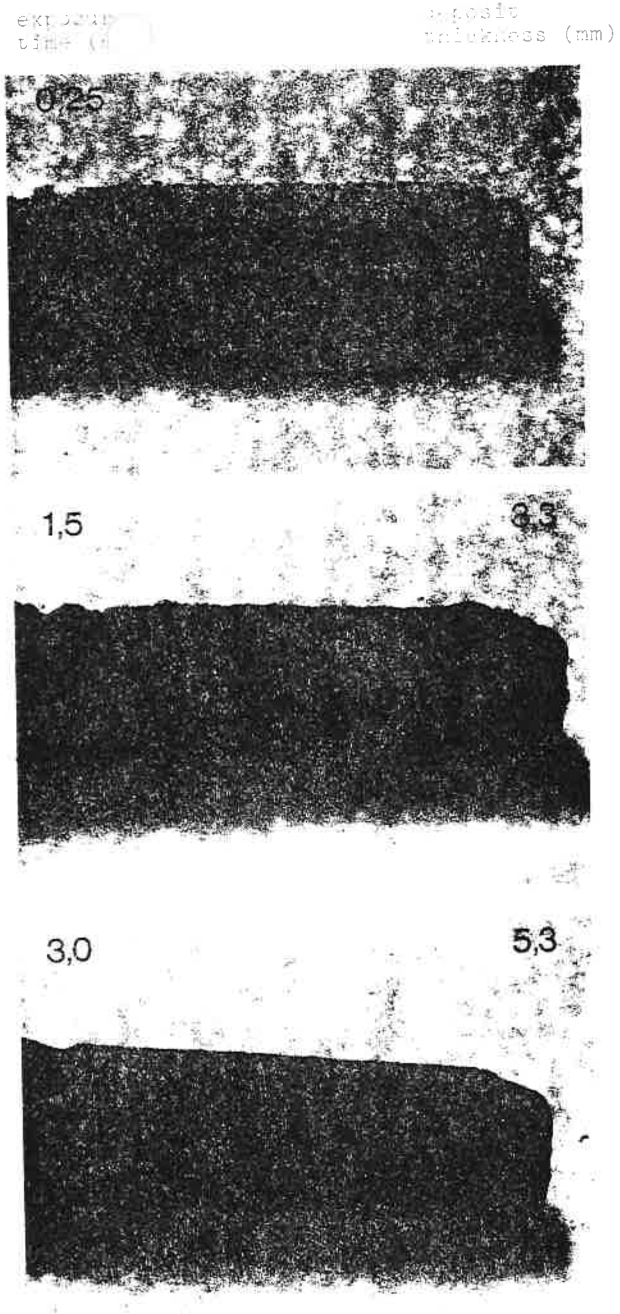


Figure [illegible]. [illegible] corrosion probe deposits from the [illegible]) sulphite boiler, b) sulphate [illegible] lower image is a magnification of the [illegible]

[illegible] particles (< 1 µm) represent [illegible]. The bigger (> 10 µm) almost [illegible]les are black liquor droplet [illegible] over from the burner level.

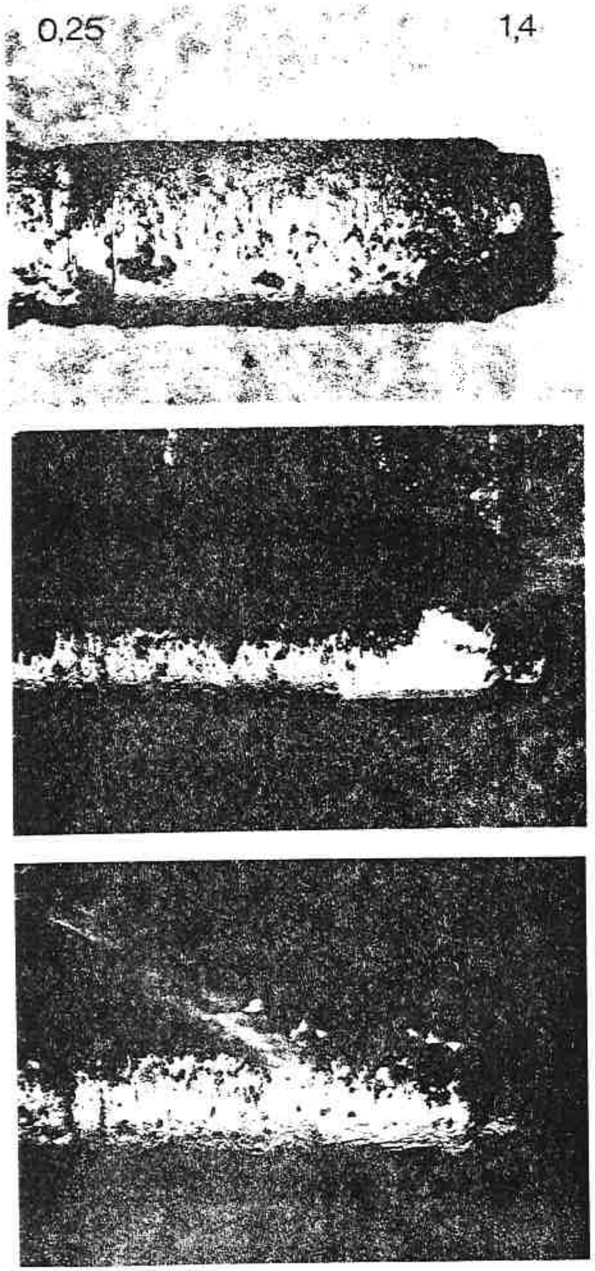


Sample ring temperature: 500 °C

SULPHATE

wood: birch
spray: spoon
O_2 : 2,3 %
Air : tangential
Liquor temp: 110 °C
Flue gas temp:
800...900 °C

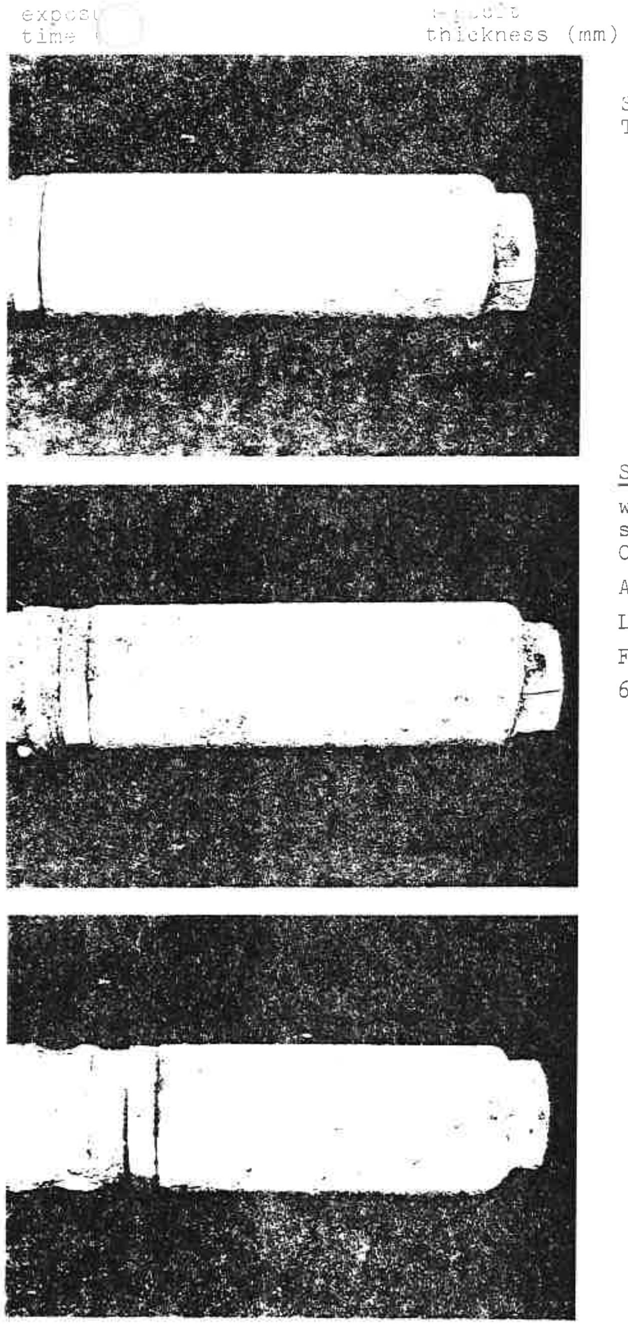
Figure 62. Deposition probe samples from superheaters. Sulphate.



Sample ring
temperature: 500 °C

SULPHITE
wood: pine+spruce
spray: spoon
O_2 : 2,3 %
Air : symmetrical
Liquor temp: 120 °C
Flue gas temp:
850...900 °C

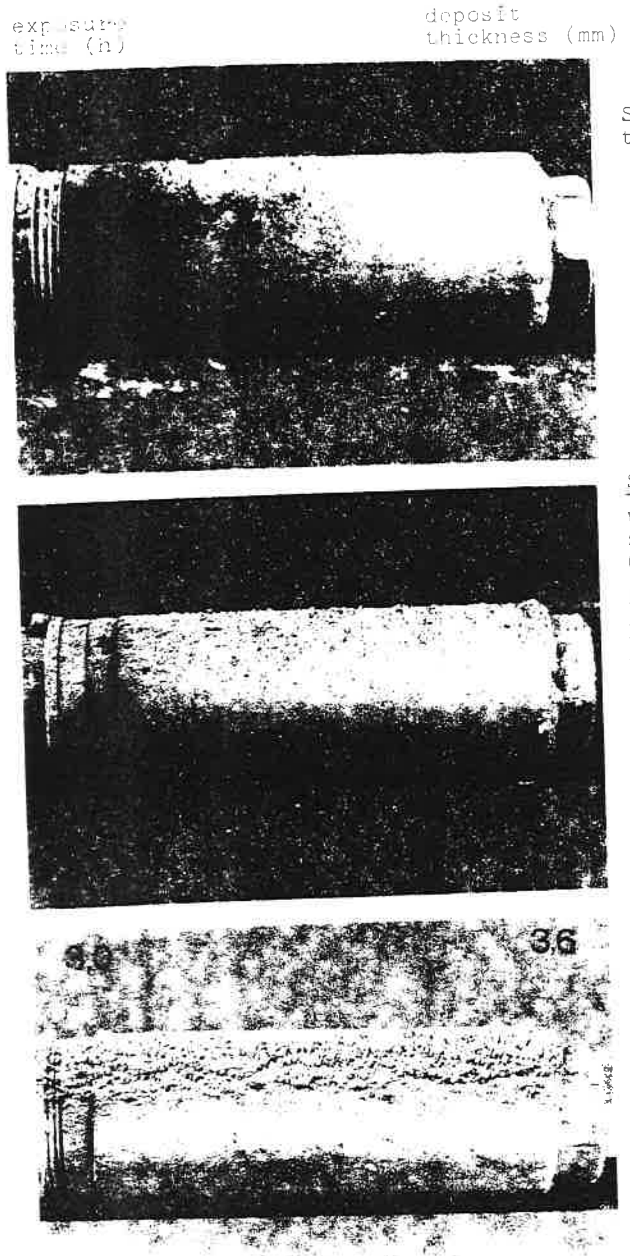
Figure [illegible] superheaters.



Sample ring
Temperature: 500 °C

SULPHATE
wood : pine
spray: spoon
O_2 : 1,2 %
Air : symmetrical
Liquor temp: 110 °C
Flue gas temp:
650...700 °C

Figure 6c. Deposition probe samples from superheaters.
Sulphate.



Sample ring
temperature: 500 °C

SULPHATE

wood : pine
spray: spoon
O_2 : 3,0 %
Air : symmetrical
Liquor temp: 105 °C
Flue gas temp:
800...900 °C

Figure [illegible]. Deposition probe samples from superheaters. Sulphate.

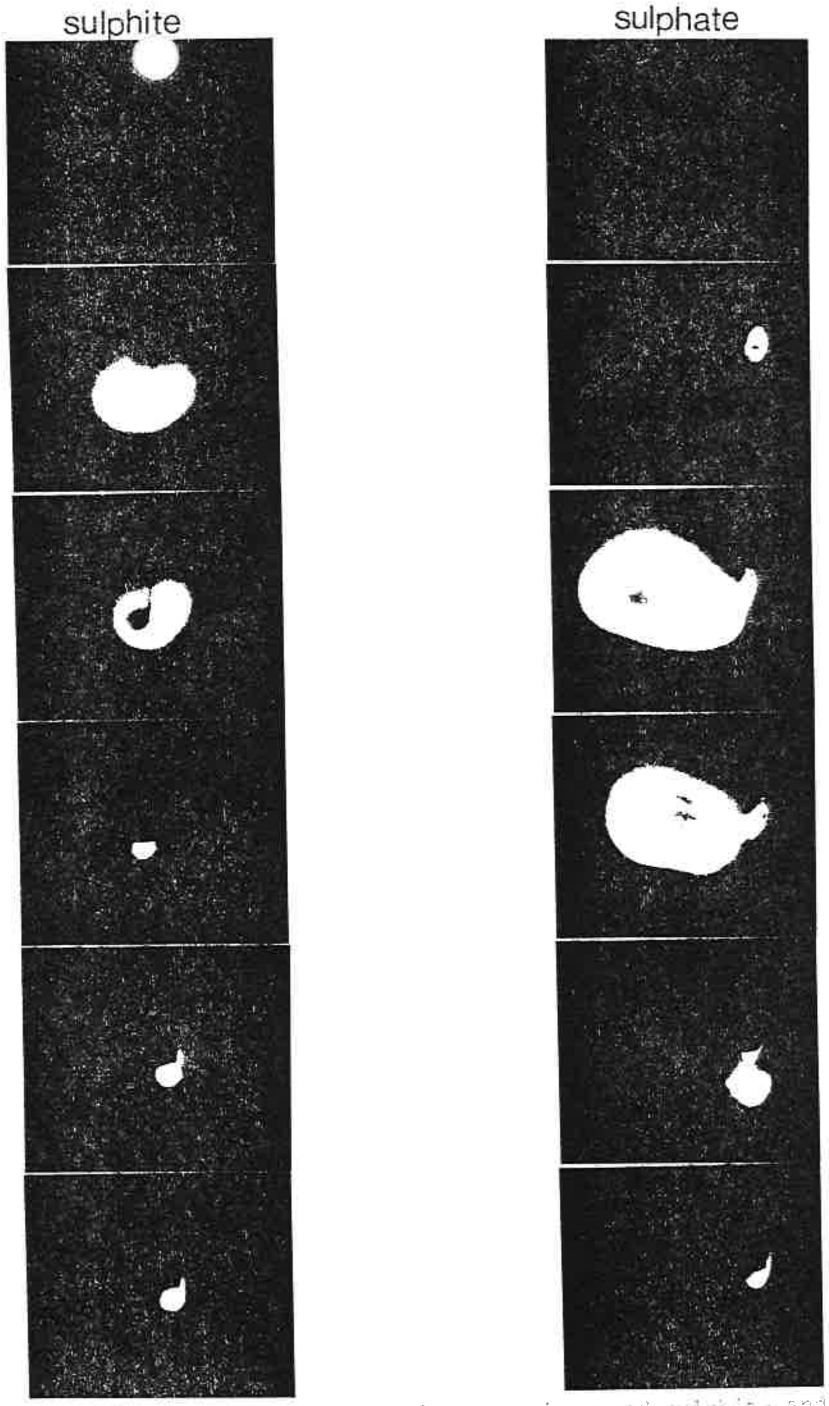


Figure [illegible]. [illegible] droplet burning experiment of sulphite and sulphate liquors. Furnace temperature [illegible]. The [illegible] seconds after insertation [illegible] in the [illegible] is indicated in each [illegible].

CHEMICAL CORROSION OF CARBON STEEL , FERRITIC AND AUSTENITIC STAINLESS STEELS BY THE GASEOUS MIXTURE N_2-H_2O-O_2-SO_2 (92.3-3.7-1.95-0.2 V %) AT 900°C : NATURE OF CORROSION LAYERS. APPLICATION TO THE CORROSION PROBLEMS IN BLACK LIQUOR RECOVERY BOILERS

J.J. RAMEAU, Professor
H. BARTHELEMY, Research Engineer

Laboratoire d'Energétique Electrochimique
associé au C.N.R.S. L.A. 265, E.N.S.E.E.G.
Domaine Universitaire, B.P. 44
-F-38401 - SAINT MARTIN D'HERES (FRANCE)

1. Abstract

The chemical corrosion by the gaseous mixture N_2-H_2O-O_2-SO_2 of a carbon steel, of 304 austenitic stainless steel and of 430 and 10 Cr-5 Al ferritic stainless steels were studied at 900°C. The corrosion products formed successive layers, the compositions of which are respectively Fe/FeS/FeO/Fe_3O_4/Fe_2O_3, 304 s.s./Cr_2O_3/Fe_2O_3, Fe_3O_4, 430 s.s./Cr_2O_3/Fe_2O_3, Fe_3O_4 and Cr-Al s.s./Al_2O_3. These results are compared to those obtained by molten Na_2S-Na_2 CO_3 corrosion tests and to "in situ" corrosion tests in recovery boilers.

2. Apparatus (Fig 1)

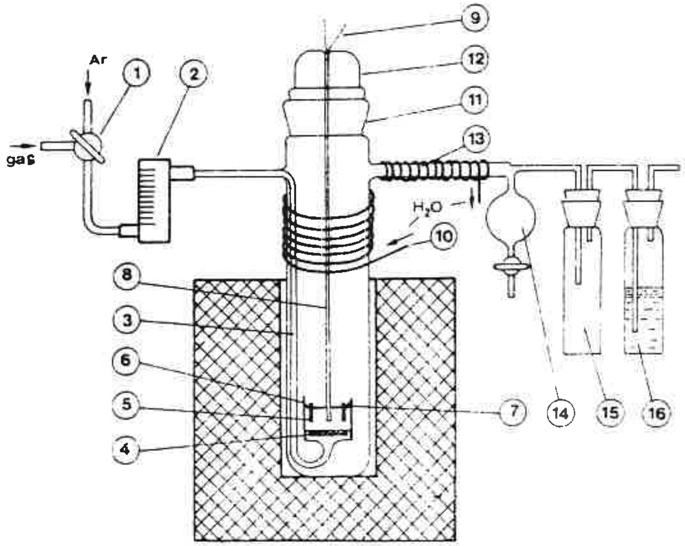


Fig. 1

Experiments were carried out in a silica air-tight cell. Corrosive gas or argon from a 3-ways cock(1)flowed through a flow regulator (2) , arrived at the bottom of the cell through the preheating tube (3) and were diffused by a sintered silica plate (4), previous to come in contact with the metallic samples (5) in the reaction chamber (6)(34 mm diameter, 60 mm high) . Four silica hooks (7) welded at the bottom of a silica sheath (8) (6 mm diameter) held the samples in position. Inside the sheath (8) was placed a Pt/Pt-Rh 10 % thermocouple (9) used for regulating the electric heater. Gases were cooled by a water circuit (10) to prevent destruction of the P.T.F.E. joint inserted between the head (12) and the body (11) of the cell. Water cooled in the output tube (13) was collected in the silica crucible (14). At last gases flowed through a watch-flask (15) and a sulfuric acid washer (16) .

We used a 10 to 30 $Nl.h^{-1}$ corrosive gas flow, the volumic composition of which, both initially at room temperature and at equilibrium at 900°C, is given in the following table

Gas	H_2O	O_2	SO_2	SO_3	H_2	H_2S	S_2
% initial	0	4	0	0	3.5	0.2	0
% equilibrium 900 °C	3.7	1.95	0.2	0.016	$2.65.10^{-6}$	$6.83.10^{-10}$	$6.64.10^{-25}$

The chemical analysis of the four different alloys tested are given in the following table

	ELEMENTS (Mass %)								
Alloy	C	Mn	Si	S	P	Ni	Cr	Al	Fe
Fe	0.062	0.70	0.20	0.022	0.035	0.30	0.20		Balance
304	0.060	1.00	0.60	0.006	0.025	8.68	18.36	0.06	Balance
430	0.041	0.35	0.39	0.006	0.022	0.16	16.24	≤ 0.0005	Balance
Cr-Als.s	0.012	0.42	0.24	0.017	0.021		10.20	5.07	Balance

The tests duration lasted from 0.25 hour to 15 hours.

3. Results

In the case of carbon steel, the mass of the sample increased with time. The corrosion products only contained iron, oxygen and sulphur. The mass of sulphur collected by the sample, m_S, was determined by chemical analysis, as a function of time. From the values of m_S, we calculated the mass of oxygen fixed, m_{O_2}. The variations of m_T^2, m_S^2, and $m_{O_2}^2$ were linear functions of time, therefore the corrosion kinetics followed a parabolic law.

X ray diffraction analysis of the corrosion products, as well as scanning electron microscopy and glow discharge spectroscopy revealed the existence of 4 successive layers :

Carbon steel / FeS/ FeO / Fe_3O_4 / Fe_2O_3 (Fig 2)
M 4 3 2 1

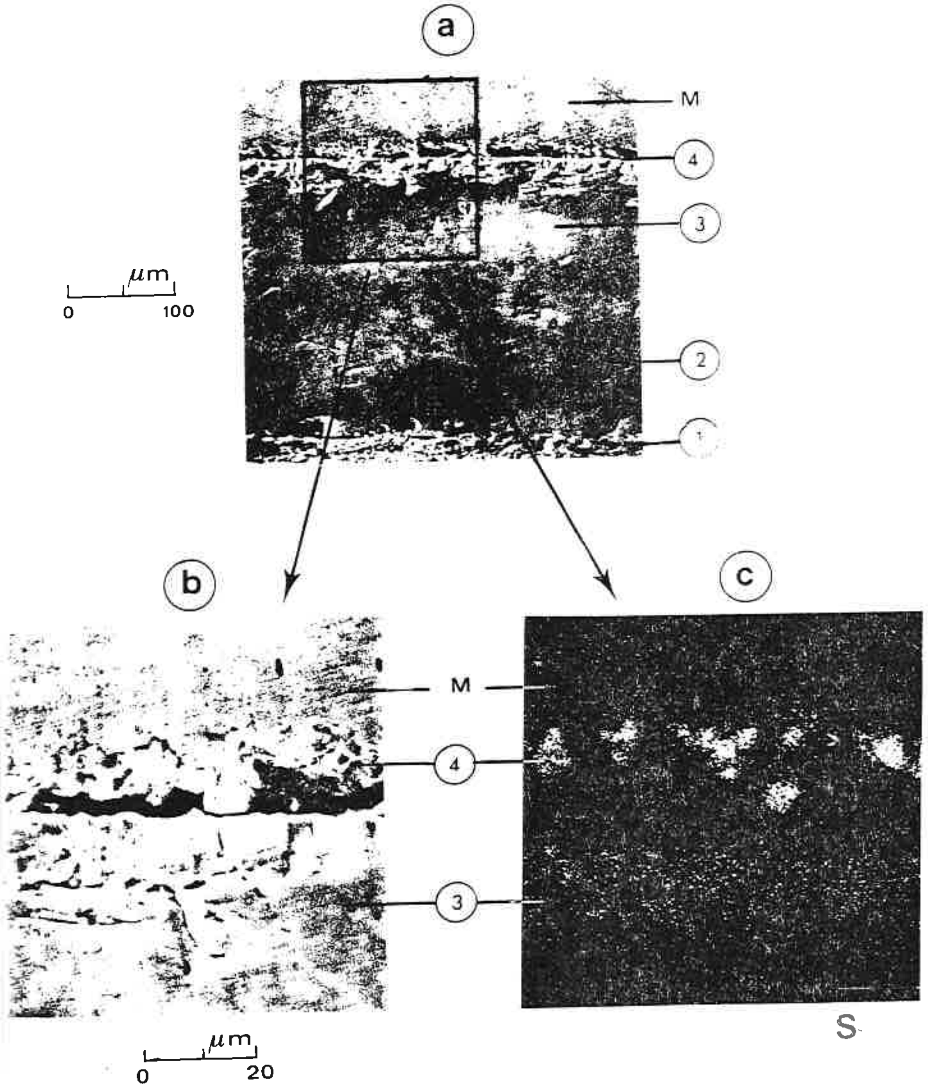


Fig. 2 Carbon steel : corrosion in gaseous mixture, 2 hours at 900°C.
Microphotos of the sections and electron probe microphotos (scanning electron microscope).
(1)=Fe_2O_3, (2)=Fe_3O_4. (3)=FeO, (4)=FeS, M=Metal (a) and (b) electronic picture;
(c) partition of sulfur.

Birks (1) observed the same type of layers in the case of iron corrosion by SO_2 between 800°C and 900°C, when the SO_2 partial pressure was superior to $2x10^{-1}$atm. The corrosion kinetics is controlled by Fe^{2+} ions diffusion in FeS and FeO, Fe^{2+} and Fe^{3+} ions diffusion in Fe_3O_4, and reverse diffusion of O^{2-} and S^{2-} ions in Fe_2O_3 and of S^{2-} in Fe_3O_4 and FeO. In the case of the 3 stainless steels, we have noticed that the mass increase remained smaller than 1 $mg.cm^{-2}$ after 70 hours. The corrosion products contained no sulphur. Examination, by means of S.E.M., of the tranverse sections of the corrosion products, for 304 stainless steel, revealed two successive layers, 5 to 10 μm thick : an internal Cr_2O_3 layer (1 μm thick) and an external Fe_3O_4 and Fe_2O_3 layer (4 to 9 μm thick).
On 430 stainless steel, the layer was essentially composed of Cr_2O_3 with a little amount of Mn_3O_4.

In the case of 304 and 430 stainless steels, we have noticed that, underneath the metal-oxide interface, there was a metal region, 3 to 5 μm thick, in which the Cr and Mn contents were lower than in the metallic matrix. It was a diffusion zone, which demonstrated the profitable influence of Cr and Mn.
On ferritic 10 Cr-5 Al stainless steel, layer was made of Al_2O_3 (.2 to .5 μm) (fig 3). Addition of aluminum was very beneficial since it hindered corrosion of the steels. Since the protective layer contained no Cr_2O_3, it seems that aluminum has a stronger anti-corrosion influence than chromium.

4. Discussion

We have also studied the corrosion of the preceeding alloys in molten Na_2S-Na_2 CO_3, which represents the salt phase in the recovery boilers at 900°C (2). The carbon steel was very quickly corroded (120 $mg.cm^{-2}.h^{-1}$) by the SO_4^{2-} ions present in the molten salt solution ; the corrosion layer contained FeS, Fe_3O_4 and Fe_2O_3. This layer was thin because iron oxides reacted with carbonate ions (3) to produce soluble FeO_2^- ions. 304 stainless steel was slowly corroded (15 $mg.cm^{-2}.h^{-1}$). The corrocion products were distributed in 3 layers : 304 stainless steel/chromium sulfide/sodium chromate with iron and nickel metal inclusions/sodium chromate. 430 stainless steel underwent quicker corrosion (18 $mg.cm^{-2}.h^{-1}$). The corrosion products were distributed in 2 layers :
430 stainless steel/ Na CrO_2, Na FeO_2 with iron metallic inclusions/$NaCrO_2$

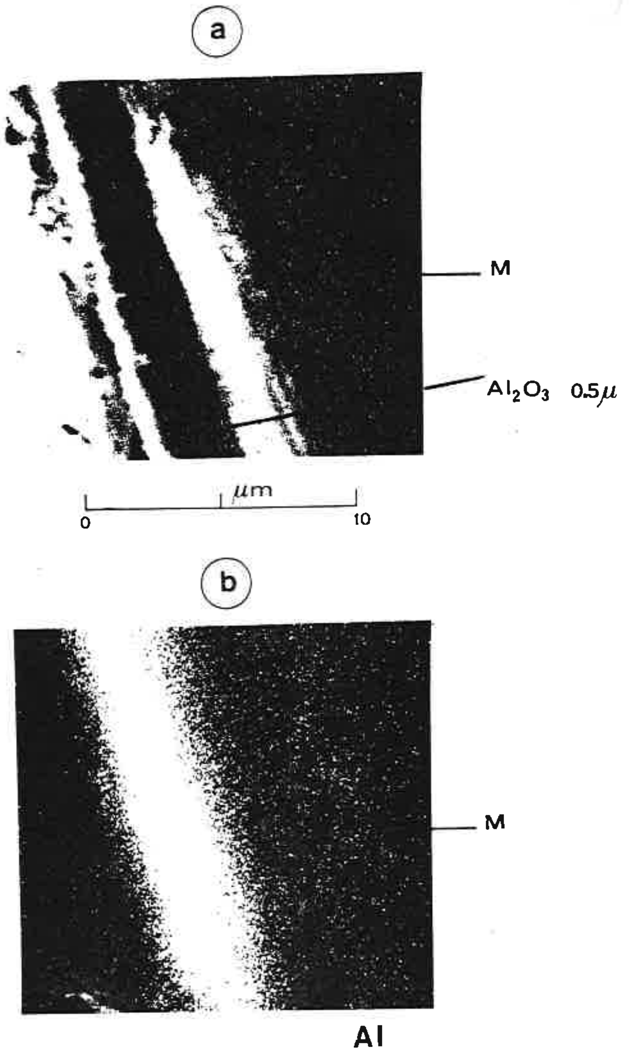


Fig. 3 Ferritic 10 Cr-5Al stainless : corrosion in gaseous mixture, 70 hours at 900°C. Micro-photos of the section and electron probe micro-photos (scanning electron microscope). M= Metal. (a) electronic picture ; (b) partition of aluminum.

The ferritic stainless steel 10 Cr-5Al was very slowy corroded ($5 mg.cm^{-2}.h^{-1}$).
The corrosion products were distributed in 2 layers :
10 Cr-5Al stainless steel/Al_2O_3 ($+Cr_2O_3$) ($NaCrO_2$,$NaFeO_2$, Fe_s,Al_2O_3 (fig.4)
We have also disposed samples of the four types of steels inside two "Combustion Engineering" recovery boilers, 1m above and .5m under the primary air nozzles, during 6 to 12 months. The carbon steel corroded very quickly (1.5 mm. year $^{-1}$). The corrosion layer was composed of FeS and Fe_3S_4 sulphides, and Fe_3O_4 and Fe_2O_3 oxides. We can explain this result by referring to our laboratory experiment(gaseous and molten salt media) : corrosion results from the simultaneous actions of gases and of molten salt throwing ups.
304 and 430 stainless steels corroded less (.4mm.year^{-1}) than carbon steel (1.5 mm.year^{-1}). The corrosion layer was composed of Cr_3S_4 and Cr_2O_3 for 304 steel, and Cr_3S_4, Fe_3S_4, Fe Cr_2S_4, Cr_2O_3, Fe_2O_3, Fe_3O_4 in the case of 430 steel. The corrosion "in situ", in both cases, was rather due to action of the molten phase than to that of the gas phase, Na CrO_2 and Na FeO_2 were not produced because the temperature was inferior to 500°C, and the reations

$$Fe_2O_3 \text{ (or } Cr_2O_3) + CO_3^{2-} \rightarrow 2\ FeO_2^- \text{ (or } 2\ CrO_2^-) + CO_2$$

did not take place (3).

10 Cr-5Al ferritic stainless steel was the best corrosion resistant (.1 mm.year^{-1}) : the corrosion layer was mainly composed of Al_2O_3 (fig5). The corrosion "in situ" was similar to that in the gaseous phase as well as that in the molten phase.

5. Conclusion

Additions of aluminum to the stainless steels compositions yielded excellent anti-corrosion results; one can take this results into account in the building of recovery boilers in two ways :
by using bi-metal tubings constituted of a carbon steel inner tube (for the mechanical strength) and a Cr-Al ferritic steel external tube.
by using carbon steel tubings covered with an aluminum based deposit.
In both cases remain the metallurgical and technological realization problems.

6. Bibliography

(1) T. FLATLEY, N. BIRKS,
Journal of the Iron and Steel Institute (1971), p. 253

(2) H. BARTHELEMY
Thesis - Grenoble (1978)

(3) N.S. STARCHIKOV
Otkrytiga Izobrut, Prom. Obraiztjy, Tovarnye Znaki, <u>50</u>, 13 (1973), p 68

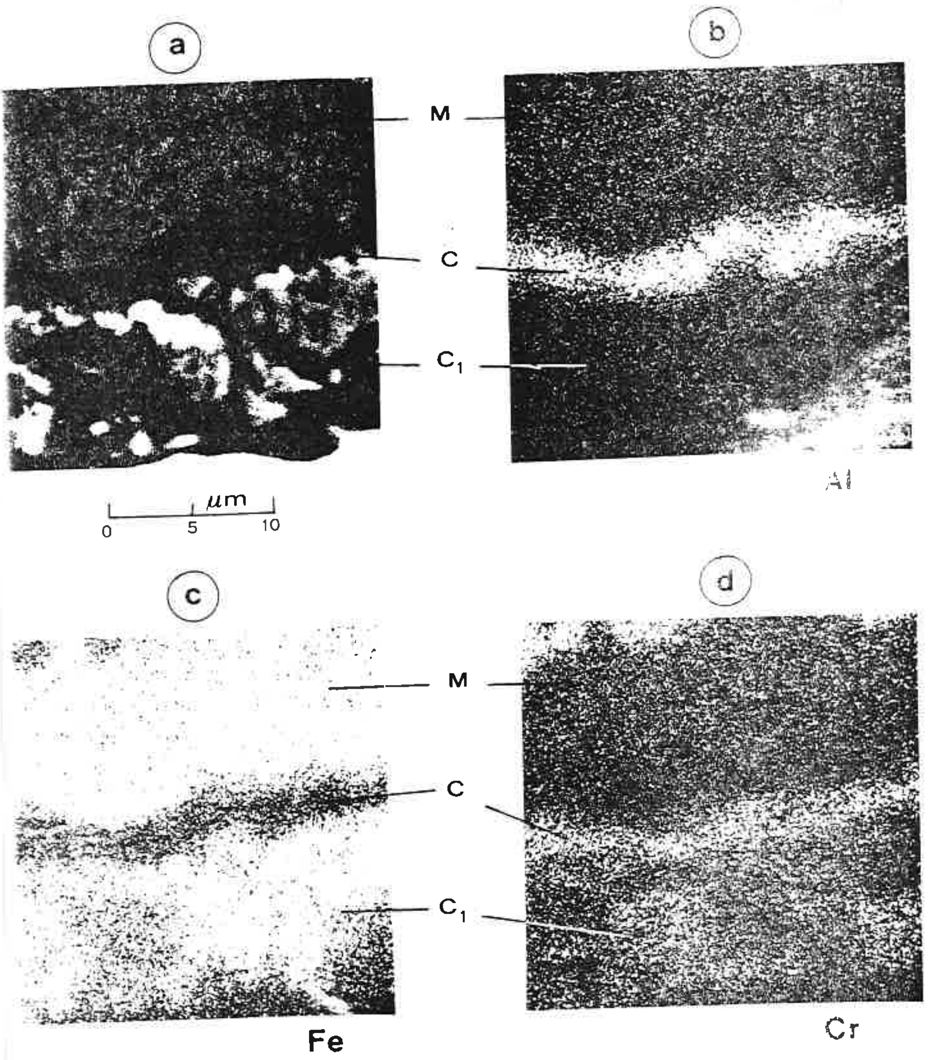


Fig. 4 Ferritic 10 Cr-5Al stainless steel : corrosion in molten Na_2S-Na_2CO_3, 15 hours at 900°C. Micro-photos of the section and electron probe micro-photos (scanning electron microscope). C_1= Na CrO_2 + $NaFeO_2$ + FeS + Al_2O_3 ; C = Al_2O_3 (+ Cr_2O_3) ; M = Metal (a) electronic picture ; (b) partition of aluminum ; (c) partition of iron ; (d) partition of chromium.

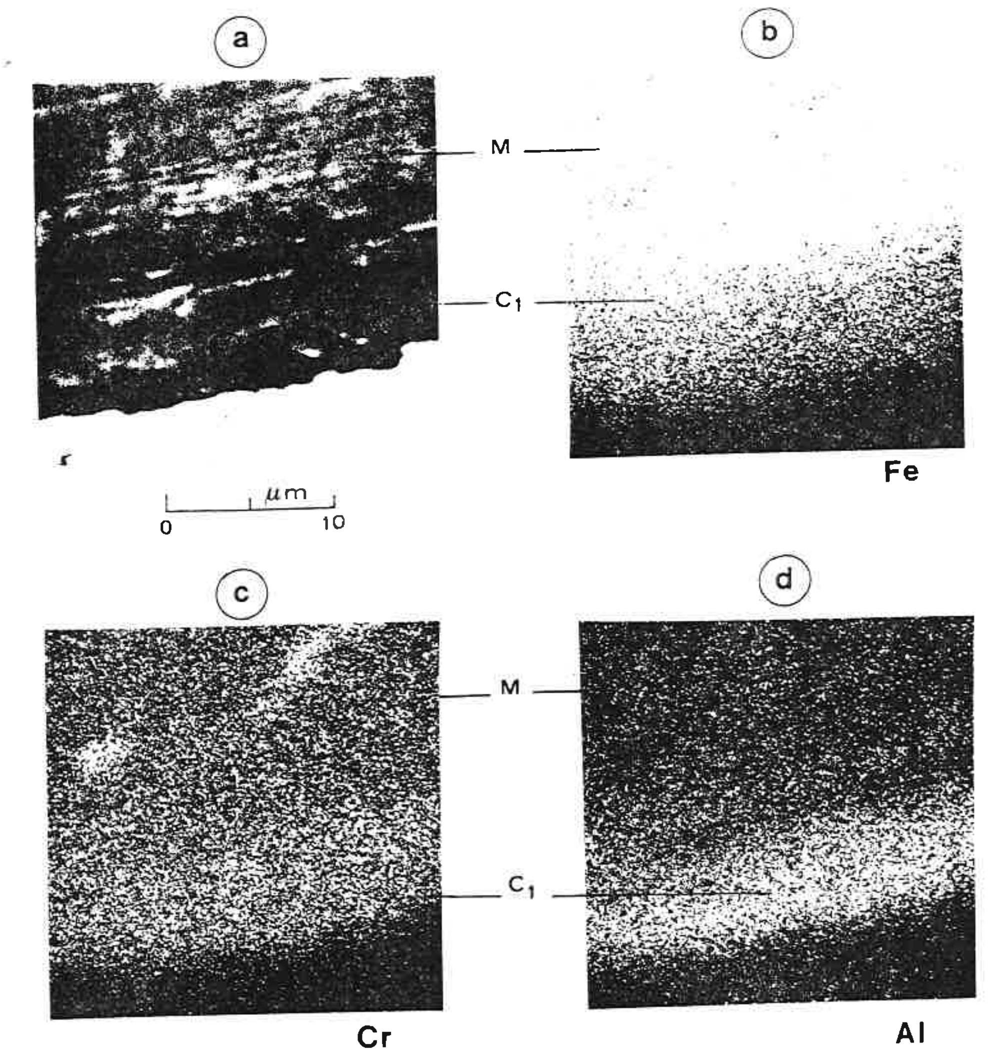


Fig. 5 Ferritic 10 Cr-5Al stainless steel : corrosion in a recovery boiler (6 months). Micro-photos of the section and electron probe micro-photos (scanning electron microscope).
M = Metal ; C_1 = Al_2O_3 (+ Cr_2O_3). (a) electronic picture ; (b) partition of iron ; (c) partition of chromium , (d) partition of aluminum.

D3 - 1

RECOVERY UNIT SUPERHEATER WASTAGE AND CONTROL--PROGRESS REPORT II

A. L. Plumley, Senior Consulting Engineer
W. R. Roczniak, Project Engineer

Combustion Engineering, Inc., Windsor, Connecticut, USA

B. E. Lefebvre, Supervisor of Industrial Design

Combustion Engineering-Superheater, Ltd, Ottawa, Ontario, Canada

1. Abstract

In the past decade, there has been increased fireside corrosion of recovery unit superheaters in recovery units with outlet steam temperatures of 900°F (482°C). There are two major ways to combat this: material changes and design changes. Traditionally, wastage has been controlled by use of higher chromium ferritic tubing and weld overlay in susceptible regions. New units have design changes that reduce the susceptibility of units to corrosion, e.g., locating the finishing superheater section out of the radiant heat region, but in some instances improved tubing materials are needed.

Two of the conspicuous causes of increased corrosion are chloride and potassium, whose levels in recovery units has increased in recent years. On the basis of the results from a controlled temperature probe test, several corroding T-22 elements in the high temperature superheater of a closed cycle recovery unit were replaced with In 800H. Integral test sections of TP 347H, TP 310H, and tubes with selected coatings were also installed to provide a more complete long range evaluation under operating conditions. The performance of the In 800H elements and some of the other alternative materials has been good, though the operating steam temperature has been held below 800°F (427°C).

New controlled temperature corrosion probe studies in both the recovery and wood waste boilers of a West Coast mill pulping salt water borne logs corroborated the previous results. Here are the conclusions:

1. While most materials show some wastage at temperatures above 950 F (510 C) the austenitic alloys, TP 304H, TP 321H, TP 347H, TP 310H, and In 800H, would improve service life in both recovery units and hogged fuel fired boilers subjected to increased chloride levels.

2. The ferritic materials, T-1, T-11, and T-22, should provide satisfactory long term service except in the highest temperature finishing loops with metal temperatures of 1000°F (538°C).

3. In the highest temperature finishing loops, the austenitic metals TP 347H, TP 310H, and In 800H would be expected to increase service life threefold.

4. In 690 and In 671 performed unsatisfactorily in the high chloride environment.

In Kreisinger Development Laboratory the waterwall region and superheater region conditions were simulated to determine the effects of chloride and potassium on the melting point of smelt. While the results indicate that sodium chloride is the dominant factor lowering the melting point of smelt and deposits, thus, increasing corrosiveness, potassium also is a factor. The results of this experiment can be used as a measure for indicating potential wastage problems.

Design changes have been introduced that reduce finishing superheater tube temperatures, improve furnace temperature/mass flow profile and control carry over, thus lowering the potential for superheater wastage.

2. Introduction

In recent years, chloride concentrations in kraft recovery boilers have increased for several reasons: pulping of salt water borne logs, waste stream incineration, and tightening or closed-loop operation within the pulping cycles.

Increased corrosion of both waterwall and superheater surfaces in recovery units has been attributed to increases in both chloride and potassium levels in combination with higher temperatures (900°F, 482°C) characteristic of many newer units. An earlier paper /1/ described a continuing study for development of superheater tubing alloys and

that would provide satisfactory furnace tube life during combustion of liquor from a closed loop pulping and recovery cycle. Smelt sampled from this boiler contained 7.8 percent chloride and 2 percent potassium as compared with about 2 percent chloride and 1 percent potassium in smelt from a typical open cycle system.

This paper provides a progress report on that effort as well as detailing the results of a new corrosion probe study conducted in a West Coast paper mill pulping logs that are transported and/or stored in salt water. The chloride and potassium concentrations approach the level found in the closed cycle operation.

In parallel with the research efforts described in this paper, design changes have been incorporated into recent chemical recovery boilers partly to offset the trends in increased wastage.

3. Background

Considerable effort has been expended during the past fifteen years by Combustion Engineering and others toward the practical prevention of waterwall wastage in chemical recovery units. Metallizing, weld overlay, composite tubing, as well as refractory retained by extended metal surface, are all procedures that have been used with varying degrees of success /2/.

Superheater wastage in recovery boilers has traditionally been controlled by the use of higher chromium containing alloys or the use of weld overlay in wastage prone areas and by arranging superheater stages in parallel flow with the hot furnace gases. Scheduled superheater replacement has sometimes been adopted as part of routine maintenance programs.

It is thought that two major adverse mechanisms may be involved in the increased corrosion rates observed in the presence of chlorides /1,3/. One involves the formation of eutectics or complexes resulting in a lowering of the melting point of deposits and subsequent fluxing of normal, protective metal oxides.

Various other impurities, such as potassium and heavy metals, can also influence deposit melting points. This phenomenon is a particular concern in waterwall wastage where the temperature range of molten smelt would be increased, thus reducing the protective capability of frozen smelt.

A second mechanism involves release of HCℓ from within tube deposits as oxidized sulfur compounds displace chloride from the deposits /4,5/. The higher operating metal temperatures in the superheater region may accelerate such behavior. Subsequent reaction may involve stepwise formation of volatile ferric chloride and/or unstable chlorides and/or oxychlorides of other alloy components.

4. Closed Loop Kraft Mill--Superheater Element Replacement

The closed-loop pulping and recovery operation initiated in Canada in 1977 produced a liquor that proved to be quite corrosive to the superheater of a 1000-ton recovery boiler producing 900°F/900 psig (482°C/6200 kPag) steam /1/. Peak metal temperatures were between 900 and 1000°F (482 to 538°C). Within a year and a half of the initial operation, significant wastage had been observed in the lower portions of the high temperature superheater (approximate metal temperature of 975°F (524°C)). Wastage continued even after reduction of final steam temperature from 900 to 710°F (482 to 377°C) through removal of superheater surface. A test program was initiated to allow selection of alternative superheater materials more resistant to the furnace environment.

On the basis of a series of controlled temperature probe test results, the lower portions of a significant number of corroding T-22 platens in the high temperature superheater of the closed cycle unit were replaced with In 800H during the fall outage in 1979 (Fig. 1). Integral 54 in. (137-cm) long test sections of TP 347, TP 310, and selected coatings that showed promise in the probe studies were also installed within the 800H replacement sections (Figure 1). The remainder of the T-22 finishing loops were replaced with In 800H within the following year.

4.1 Test Results

After installation of the In 800H tubing it was decided to increase the

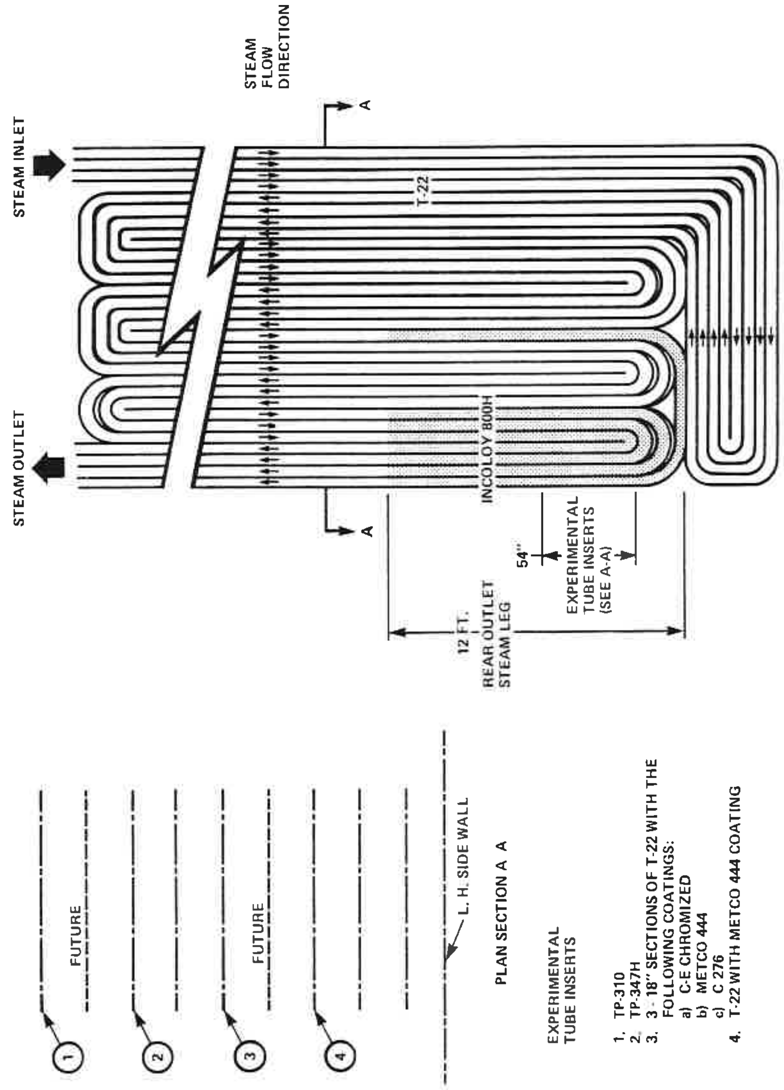
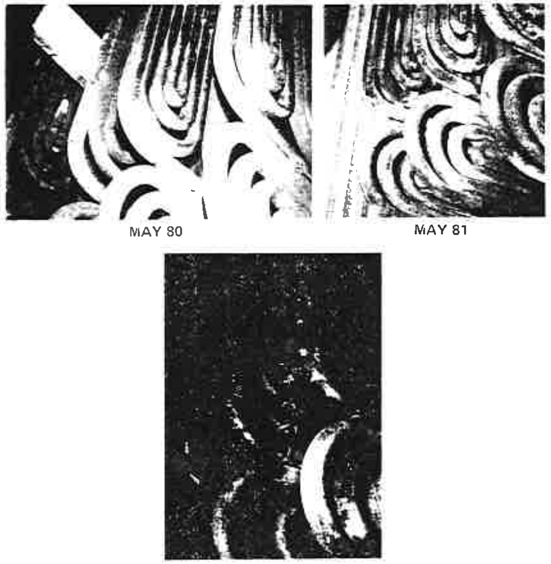


Fig. 1: Twenty-nine (29) Incoloy 800H replacement sections in finishing superheater (Detail of Fig. 12a)

superheater outlet steam temperature stepwise by regulation of interstage desuperheater spray to a level where wastage was controllable rather than returning to the design temperature of 900°F (482°C). Thus the steam outlet temperature was decreased to 710°F (377°C) from September 1979 till May 1980 and then gradually increased to 740°F (393°C) where it remained through December 1981. Steam temperature since then has approached 800°F (427°C).

Periodic inspections have been made of the In 800H elements and the test sections of TP 310, TP 347 and coated T-22. Visual observations together with ultrasonic monitoring by the customer has shown that the In 800 platens are generally in good condition with only surface darkening or slight roughening (Figure 2). The TP 347 and TP 310 sections installed in the vertical outlet legs showed little indication of corrosion.

Integral test sections of T-22 plasma coated with Hastelloy C-276 and

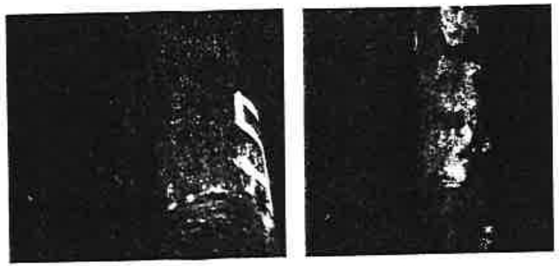

MAY 80

MAY 81

NOVEMBER 81

Fig. 2: In 800H platen assembly during sucessive inspections

Metco 444 and a length of C-E chromium diffused T-22 were also installed. No significant changes were found in these test platens except with the Metco 444, which showed noticeable loss of the coating layer within one year and attack of the base metal after only two years (Figure 3).


HASTELLOY C276

METCO 444

Fig. 3: Test sections after exposure

Trends in wastage of the In 800 and other materials may be seen in a plot (Figure 4) of wall thickness loss measurements obtained during various inspections of the superheater.

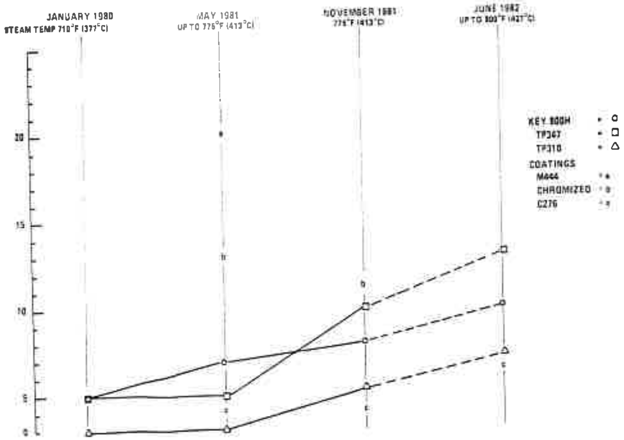


Fig. 4: Wastage trends in replacement assemblies

5. Corrosion Probe Study in West Coast Recovery Boiler

5.1 Experimental Procedures

The design and operation of superheater corrosion probes has been described in published reports /1,2,6,7/. For this study 18 test specimens were nested together to form the air-cooled "test superheater element." The test probe specimen temperatures were regulated and monitored by means of thermocouples embedded in the specimen walls. A temperature gradient along the length of the test probe enabled the evaluation of a given metal at more than one temperature.

Results from the previous controlled temperature probe study suggested that conventional superheater tube materials (T-11, T-22) would not provide more than a few years of service in a high chloride system at metal temeperatures above 900^{o}F (482^{o}C). The 2000-hour study was initiated to determine whether alternative alloys or coatings could provide adequate service life under similar conditions. Table I shows the compositions of the various alloys used on the corrosion probe. Figure 12a shows the typical location of the probe in the boiler.

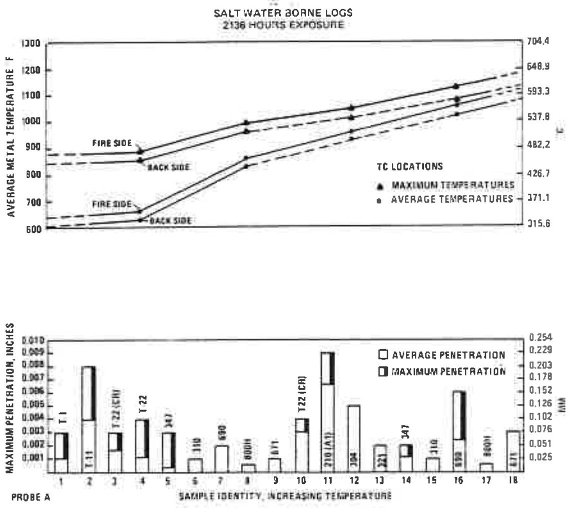


Fig. 5: Penetration vs temperature profile for probes in recovery boiler

Table I
TEST PROBE SAMPLE COMPOSITIONS
(% by weight)

	Cr	Ni	Fe	Mo	Mn	Si	C(max)	Other
SA 192	----	----	98.4	----	0.63	0.25	0.18	----
SA 210*	----	----	97.0	----	----	0.10	0.27	----
T-1	----	----	97.8	0.65	0.80	0.50	0.20	----
T-11	1.25	----	96.5	0.55	0.45	0.75	0.15	----
T-22	2.25	----	95.0	1.0	0.45	0.50	0.15	----
TP 304H	18.0	8.0	74.0	----	----	----	0.08	----
TP 321H	18.5	11.0	67.7	----	2.00	0.75	0.10	----
TP 347H	19.0	12.0	69.0	----	----	----	0.08	Nb-1.0
TP 310H	25.0	20.5	54.0	----	----	----	0.25	----
In 800H	21.0	32.0	46.0	----	1.5	1.0	0.10	Al-0.60
In 690	30.0	60.0	9.5	----	----	----	0.03	----
In 671 clad on 800H	48.5	51.0	----	----	----	----	0.05	Ti-0.35
C-E Chromized on T-22	97 + oxides	----	----	----	----	----	0.05	----

* SA 210 sample was aluminized

5.2 Test Results

The test probe was removed after 2136 hours of actual kraft recovery furnace operation burning black liquor. The penetration measurements are shown in Figure 5 relative to a skin metal temperature profile recorded from the probe thermocouples during the exposure.

In general, an increase in corrosion resistance was observed with increasing chromium content of the alloy; however, the high nickel alloys, Inconel 690 and Inconel 671, were unsatisfactory despite high chromium content. This observation is consistent with the known inability of initially formed nickel sulfide to provide further protection in a high sulfur "reducing/oxidizing" environment. Figure 5 also shows the trend for increasing wastage with increasing temperatures.

In Figure 6 selected cleaned specimens are shown reassembled in the same sequence as on the probe during exposure. Also shown are detailed 7X magnification photographs. Ferritic materials tend to exhibit general wastage on the entire sample circumference while the austenitic and high chromium nickel alloys are more locally attacked. While suffering only slight general wastage, the TP 304H sample was particularly deeply pitted in some areas.

Examination of chromized T-22 indicated good corrosion resistance at lower metal temperatures. However in the 900 to 1000°F (482 to 538°C) range neither the chromized nor aluminized tubing appeared likely to provide adequate long term protection.

Analyses of deposits removed from individual coupons are summarized in Table II. Potassium concentration generally decreased while chloride concentrations in both the gross deposits and inner layers were found to increase with increasing probe surface temperatures. This trend shows an increase in corrosion potential with increasing temperature of metals in contact with such deposits. These deposits containing noticably more chloride than the general trend were also found lower in sulfur.

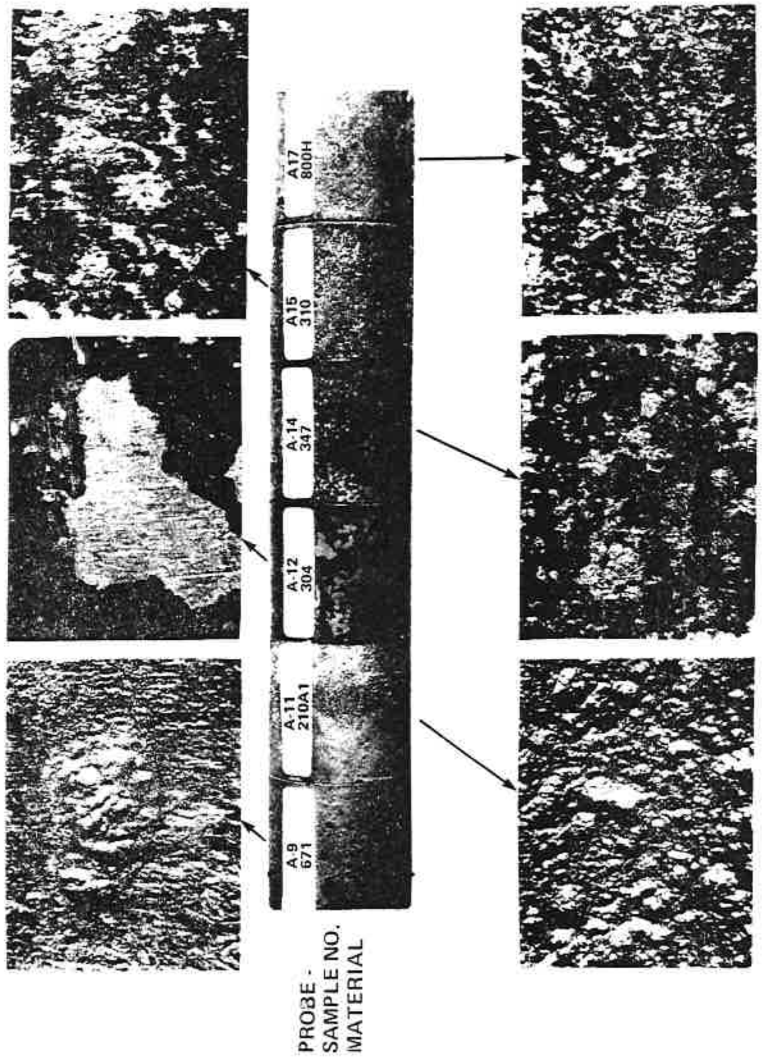


Fig. 6: 7X magnification of exposed recovery boiler samples after cleaning

Table II
ANALYSIS OF RECOVERY UNIT PROBE
SAMPLE DEPOSITS
(Weight %)

				T-1	T-11	T-22(CR)	T-22	347	310	690	800	671	T-22(CR)	210(AL)	304	321	347	310	690	800	671
Sample ID	Bulk Deposit Cold End	Bulk Deposit Hot End	Smelt	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
C	0.9	1.0	1.5																		
Gross Deposit																					
Na	31.9	32.2	38.9	30.5	30.0	31.3	30.9	31.1	30.2	31.1	30.2	30.2	30.5	30.9	31.1	30.4	30.6	30.6	30.8	31.3	29.9
K	1.0	0.8	1.6	2.1	2.6	1.6	1.9	1.7	1.4	1.4	1.5	1.4	1.8	1.6	1.1	0.9	0.7	0.6	0.7	0.8	0.6
$CO_3^=$	4.4	6.5	33.1																		
Cl	11.0	12.0	8.5	12.9	8.1	13.9	14.9	13.5	14.8	15.2	16.4	15.1	18.2	19.7	18.2	14.9	11.4	14.7	29.1	26.2	2.5
total S as $SO_4^=$	52.6	50.5	17.0	49.7	53.9	44.8	46.6	45.3	43.4	45.2	44.9	46.3	41.5	40.8	41.8	45.1	48.0	45.4	28.1	30.2	53.0
Inner Layer																					
S							15.4	16.2	16.4	14.7	12.4	24.3	18.0	11.9	12.4	13.7	13.3	14.2	8.35	6.57	8.68
Cl							1.95	8.86	14.8	11.7	14.5	11.3	15.9	21.4	24.6	29.4	23.0	17.6	16.0	32.3	10.8
K							3.72	4.28	4.83	4.94	3.77	4.41	6.02	5.65	3.46	2.5	1.76	0.83	1.94	0.87	0.54
Al													<0.1	<0.1	<0.1	--	--	--	--	--	--
Cr													0.27	0.1	<0.1	<0.1	<0.1	0.14	3.75	<0.1	3.22
																	<0.03	0.26	9.05	<0.03	14.8

Bulk deposit melting point: initial: 1095-1115°F (591-602°C)
final : 1410-1440°F (766-782°C)

As referred to earlier, other investigators have postulated that chloride is released from deposits to the gas stream as $HC\ell$ when SO_2 is assimilated /4,5/.

5.3 Conclusions

(1) As might be expected, the overall corrosion rate after 2136 hours leveled off significantly from that found in the 870-hour test. Therefore, superheater wastage of this type is not linear with time, but is repressed by protective oxide layers that build up on the heated metal surface.

(2) The austenitic alloys TP 321H and 347H should provide adequate long term service at metal temperatures 975 to 1000°F (523 to 538°C) corresponding to 900°F (482°C) steam temperature. Alloys TP 310H and In 800H could be expected to provide superior corrosion resistance at even higher temperatures. If stress corrosion type failure is a concern due to the possibility of contaminated boiler water in the superheater, then either TP 310 composite over T-22 or In 800H would be superior to the austentic alloys mentioned above.

(3) Alloys In 690 and In 671 would not be satisfactory if used in this service for any extended period of time. Even though the exposed TP 304H sample suffered only slight weight loss, this alloy was subject to localized pitting, which could result in tube failure if the wastage continued. Neither chromized nor aluminized tubing appeared to provide adequate long term protection at 900 to 1000° (482 to 538°C) metal temperatures.

6. Corrosion Probe Study in Hogged Fuel Boilers

Similar accelerated corrosion behavior has been observed in units burning bark from salt-water borne logs. In one such installation deposits containing over 42 percent sodium chloride were collected. In this case, a redesign of superheater circuitry with partial flow reversal resulted in a skin metal temperature reduction of 200°F (111°C) from the original 950 to 1000°F (510 to 538°C) in the region where wastage had previously been severe.

6.1 Experimental Procedure

To provide in-service experience in an existing bark burning unit, with materials for possible replacement superheater elements, a controlled temperature corrosion probe study with 18 test specimens was carried out.

6.2 Test Results

Penetration measurements, made on the individual specimens following a cleanup with inhibited hydrochloric acid to remove remaining deposits and oxide layers, are presented graphically in Figure 7, along with metal temperatures. In general, it can be seen that corrosion increases with temperature and tends to decrease with increasing chromium content.

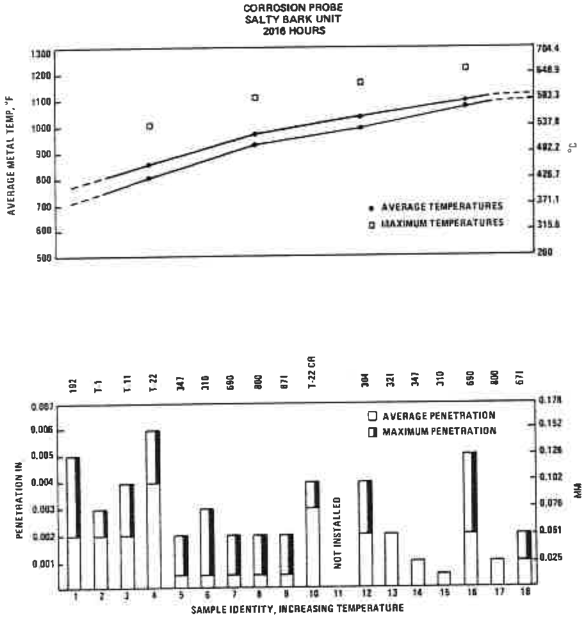


Fig. 7: Hogged fuel fired boiler penetration vs temperature profile

On the basis of these tests, the ferritic materials do not appear satisfactory for long term operation in this environment much above 850°F (454°C). The austenitic alloys, TP 304H, 321H, 347H, however,

would provide long (superheater) life at outlet steam temperatures approaching 900°F (482°C) (950 to 1000°F (510 to 538°C) metal temperature). Because of pitting in TP 304H we suggest limiting its use to regions of low corrosion potential.

6.3 Conclusions

For prolonged use at higher tempereatures, TP 310H, In 800H, and possibly In 671 clad should provide superior corrosion resistance. These studies suggest that TP 310H is slightly more resistant than the other two materials.

If stress corrosion failure is a concern due to the possibility of contaminated boiler water, then either TP 310 clad over T-22 or use of In 800H should be considered rather than any of the 300 series austenitic alloys alone.

Despite excellent performance at temperatures below 1000°F (538°C) In 690 showed a tendency for deterioration at higher temperatures and cannot be recommended for extended use in this service.

7. Furnace Corrosion Screening Bench Test

7.1 Background

The effects of increased chloride levels on boiler tube wastage has been reported in the literature for many years. For several years ongoing laboratory studies have been conducted at C-E's Kreisinger Development Laboratory (KDL) to understand and quantify factors affecting tube wastage. The present study was initiated to determine the corrosive limits of sodium chloride and potassium due to the serious wastage problem encountered in a boiler operating with a closed pulping and recovery cycle. This mode of operation allows impurities to concentrate in the recovery unit. Analyses of smelt and deposit samples obtained from the unit experiencing this wastage revealed significant increases in two constituents: sodium chloride and potassium. Actual deposits containing 1 to 2 percent of these constituents showed a significant depression of melting point. The corrosion potential of smelt mixtures under both superheater and waterwall conditions was evaluated. The results from this study are similar to those reported by University of Toronto investigators /5/.

7.2 Experimental Procedures and Test Results

The first step in this study was to prepare a series of synthetic smelts in which the concentration of potassium was increased up to 6 percent. These batches were free of sodium chloride. The addition of 2 percent potassium depressed the melting point approximately 100 Fahrenheit degrees (55 Celsius degrees). The melting point is further depressed by a total of 150 Fahrenheit degrees (83 Celsius degrees) with increasing potassium content, but at a significantly slower rate and appears to plateau between 4 and 6 percent potassium. With all these synthetic smelts, an initial melting occurred followed by a completely molten stage at about 100 Fahrenheit degrees (55 Celsius degrees) above the initial melting point.

The second phase of testing consisted of preparing synthetic kraft smelts composed of 2 and 4 percent potassium with varying concentrations of sodium chloride. The effect of these impurities on the melting points were determined for each batch of synthetic smelt (Fig. 8). Both the initial melting and the final completely molten condition temperatures are shown. The ΔT between the initial melting and the final melting point appears to be influenced by the sodium chloride concentration. Smaller differences were observed due to the potassium concentration only.

Corrosion rates of SA 192 carbon steel in 18% Na_2S synthetic smelts containing potassium without sodium chloride were determined at two different temperatures. The lower temperatures of $700^{o}F$ ($371^{o}C$) typifies the metal temperature of waterwall tubes. The higher temperature of $1000^{o}F$ ($538^{o}C$) corresponds to the superheater metal temperature. Figure 9 shows these corrosion rates for both temperatures. The shape of the wastage curve for these smelts is similar to the curve obtained using synthetic smelt containing only sodium chloride. The effect of

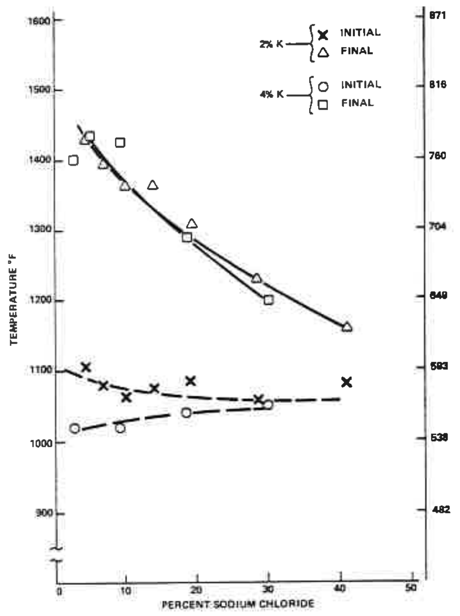


Fig. 8: Effect of sodium chloride on smelt melting point containing 2 and 4 percent potassium

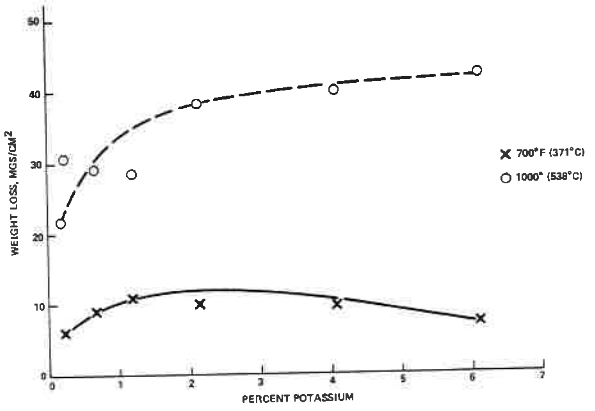


Fig. 9: Corrosion rate of SA-192 as a function of potassium content in synthetic smelt

potassium and sodium chloride on the corrosion rate of carbon steel SA 192 (Fig. 10) is approximately the same as that obtained with sodium chloride. In both cases, corrosion increased with temperature, as anticipated.

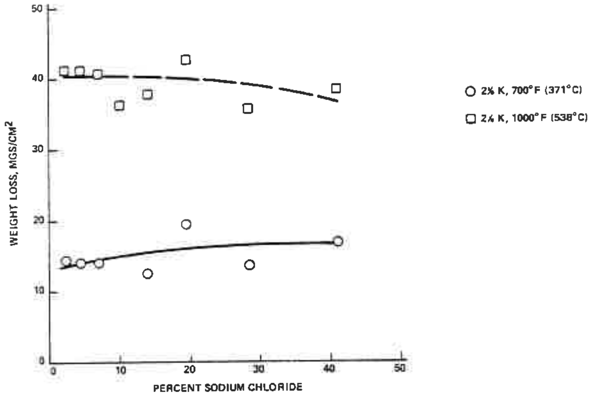


Fig. 10: Corrosion rate of SA-192 as a function of sodium chloride in synthetic smelt containing 2 percent potassium

Included in Figure 11 are the corrosion rates with increasing sodium chloride concentration at 4 percent potassium levels at 1000°F (538°C)

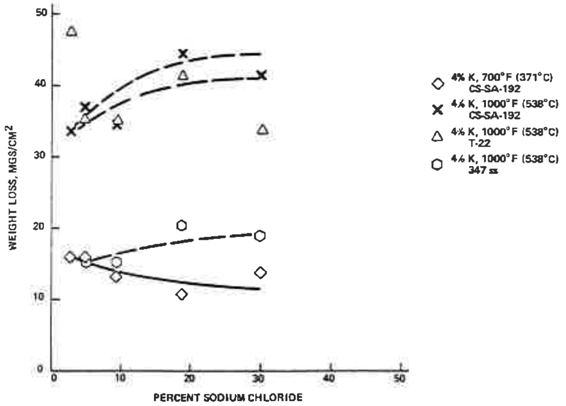


Fig. 11: Corrosion rates of SA-192, T-22 and TP 347 as functions of sodium chloride in synthetic smelts containing 4 percent potassium

for T-22 and 347 ss compared with that for carbon steel. Very little improvement in corrosion rate is noted between carbon steel and T-22 under these test conditions. The corrosion rate of 347 ss at 1000°F (538°C) is similar to the corrosion rate of carbon steel at 700°F (371°C).

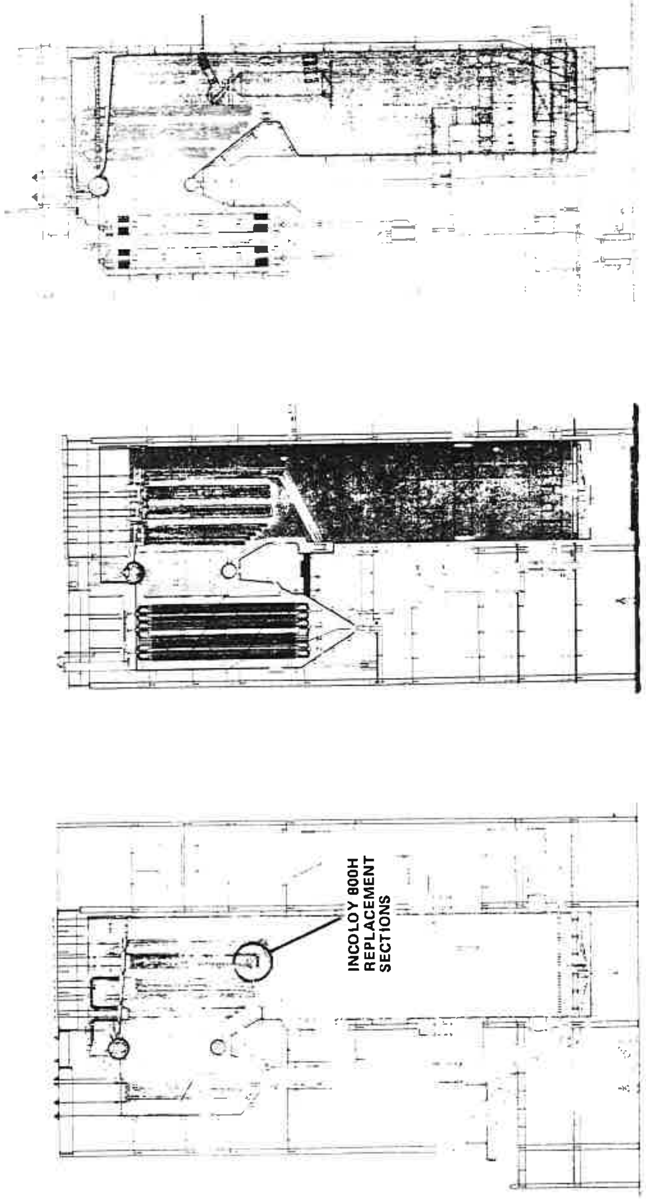
7.3 Conclusions

Sodium chloride appears to be the dominant factor decreasing the melting point of synthetic smelt up to concentrations of 20 percent. The influence of potassium on the melting point appears to peak out near 4 percent. The synergistic effect of sodium chloride and potassium on the corrosion rate due to increased potassium is minimal at 1000°F (538°C). The corrosion rate of austenitic steel (347 ss) is approximately 50 to 60 percent less than carbon or low alloy steels under the same test conditions.

8. Design Changes

Design changes have been incorporated into recent chemical recovery boilers partly in response to the increased wastage potential in parallel to the search for better materials. A number of these changes are apparent if one compares the furnace arrangements shown in Figure 12 a, b and c.

The superheater stages are arranged in parallel to the flow of hot furnace gases and the finishing superheater section is out of the radiant heat region. This minimizes the maximum metal temperature for a given final steam outlet temperature, thereby reducing the potential for increased wastage. Interstage desuperheating is also recommended. Units designed for steam conditions of 900°F (482°C) and higher have little need for additional radiant saturated surface in the form of screens, as the superheater is usually large enough to lower the flue gas temperature entering the generating bank to an acceptable level. To minimize the amount of direct radiation on these superheaters, the furnace height is extended 15 to 25 feet (5 to 8 meters) with the finishing superheater located behind the nose. (See Fig. 12c.)



c
New design

b
New design

a
Early design

Fig. 12: Trends in recovery boiler design

The secondary air nozzles are now located in the corners of the furnace to provide optimum utilization of the full furnace cross-section and to avoid rising cold channels of flue gases in the corners. An improved temperature/mass flow profile across the superheater inlet has been observed. Side to side steam temperature variations have been reduced to less than 50 F (28^{o}C). (See Figs. 12b and c.)

In an effort to provide good lower furnace combustion and improve overall chemical reduction efficiency bi-level primary air introduction has been incorporated on new units. About 75 percent of the primary air is introduced into the bed at the conventional angle with a velocity of 160 fps (50 m/s) while the remaining air is introduced horizontally at a second elevation about 1 meter higher than the first. This air at 200 fps (60 m/s) provides improved bed control (due to increased air penetration), and results in more complete burnout of volatiles, better control of reduction efficiency, and less carryover of solids into the superheater. Wastage, plugging potential and emissions are reduced.

9. Summary

Except for the rather unsatisfactory performance of the In 690 and In 671, all the austenitic alloys would improve service life in both recovery units and hogged fuel fired boilers subjected to increased chloride levels. The ferritic materials T-1, T-11, and T-22 included should provide satisfactory long term service except in the highest temperature finishing loops with metal temperatures 1000^{o}F (538^{o}C) where the austenitic materials TP 347H, TP 310H and In 800H would be expected to provide as much as a threefold increase in service life.

The sodium chloride and potassium levels found to accelerate wastage are useful in providing an advance indication of potential wastage problems.

Design changes have been introduced that reduce finishing superheater tube temperatures, improve furnace temperature mass flow profile, and control carryover, thus lowering superheater wastage potential.

1. K. W. Morris, A. L. Plumley, and W. R. Roczniak, "The Effect of Chlorides on Recovery Unit Superheater Wastage: an R & D Progress Report," paper presented at the Third International Symposium on Pulp and Paper Industry Corrosion Problems, Atlanta, GA, May, 1980; Combustion Engineering Publication TIS-6508A, 1000 Prospect Hill Road, Windsor, CT 06095.

2. A. L. Plumley and W. R. Roczniak "Recovery Unit Waterwall Protection," TAPPI 58 Spetember 1975, Vol. 9; also available as Combustion Engineering publication TIS-4316.

3. R. W. Borio, A. L. Plumley and W. R. Sylvester, "Control of High Temperature Metal Wastage in Pulverized Coal-Fired Steam Generators," paper presented at Engineering Foundation International Conference on Ash Deposits and Corrosion due to Impurities in Combustion Gases, Henniker, NH, June 26-July 1, 1977, Combustion Engineering publication TIS-5055, Windsor, CT.

4. D. A. Vaughan, H. H. Krause, and W. K. Boyd, "Chloride Corrosion and its Inhibition in Refuse Firing," Ash Deposits and Corrosion Due to Impurities in Combustion Gases, ed. Richard W. Bryers, Hemisphere Pub. Corp., 1978.

5. Reeve, P. W., Tran, H. N., and Barham, D., (University of Toronto) "Superheater Fireside Deposits and Corrosion in Kraft Recovery Boilers," TAPPI 64, May 1981, p 109.

6. A. L. Plumley, J. Jonakin and R. E. Vuia, "A Review of Fireside Corrosion in Utility & Industrial Boilers," Canadian Chemical Processing 51, 52 June and July 1970; also available as Combustion Engineering publication TIS-2775, Windsor, CT.

7. A. L. Plumley, J. A. Burnett, and V. Vaidya, "An Update of Fireside Corrosion in Utility Boilers," paper presented at the Canadian Institute of Mining and Metallurgy Toronto August 29-September 3, 1982, Combustion Engineering publication TIS-7149, Windsor, CT.

8. B. Warnquist and R. Bernhard, "Removal of Chloride From Recovery Systems by Reaction with Sulfur Dioxide," Paper and Timber, 1975, No. 8.

CERAMIC SMELT SPOUTS FOR RECOVERY BOILERS

by

B. Thorström, Managing Director
Termorak Oy, Helsinki, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

CERAMIC SMELT SPOUTS FOR RECOVERY BOILERS

Börje Thorström, Managing Director

TERMORAK OY, Helsinki, Finland

Metal plate construction spouts are nowadays used for liquid flow from recovery boiler furnace to mixing tank. The usual analysis for liquid is:

Sodium carbonate	76 %
Sodium sulphide	21 %
Sodium sulfate	1 %
Sodium hydroxide	1 %

\+ small amounts of sodium sulphite and sodium chloride

Due to their water cooling system the spouts cause a considerable risk for the general operating safety of recovery boilers. The particular risk factor is so kalled smelt explosion. The smelt explosion is caused when liquid comes into contact with water; the liquid with high heat capacity evaporates water with enormous speed. In normal circumstances is the temperature of liquid around 800...850°C, so if metal plate construction spouts are used, water cooling is essential.

Usually cooling water runs in the spout with cravity circulation principle that is why its complete effect does not cover all parts of the spout. Due to this fact heavy stress will occur in metal plate constuction spouts which have been the reason for breaking of welded joints.

The water cooling system is composed of pumps, piping and tank why its building and maintenance costs are relatively high. Worth noticing is as well the fact that chemically purified boiler water is used as cooling water.
On the basis of above described facts can two disadvantages be mentioned: a) operating safety and
b) expensiveness of the system.

Ceramic smelt spout

Termorak Oy has constructed a smelt spout which is made of ceramic material and is totally noncooled. The basic construction is formed by metal framing and ceramic lining inside.
The used ceramic material and the applied casting method quarantee the fact that the spout withstands temperature of the liquid and its chemical effects.

The spouts are made so that they can be installed to existing fixing system without that it would be necessary to make any changes to smelt openings.

For warming the longest spouts are equiped with fluid gas burners. Warming may be needed when the boiler is heated up to avoid congealment of chemical smelt. The congealment is caused when the spout is cold and liquid flow is not continuous, thus liquid does not warm the spout enough.

Consequently, it can be concidered that the problem with spouts has been solved in reverse principle than previously; earlier the spouts were cooled today they are heated.

The congealment of liquid is very common as the kinematic viscosity in 90°C is about 80 cSt and in temperature of 140°C about 10 cSt. This is the reason why it is substantial to take care that temperature in the spout is high enough.
In case the liquid congeals in the spout it has to be removed mecanically which is harmfull to the ceramic construction.
Heating of the spout is so a better alternative.

During normal run, when liquid flows continuously, temperature of the spout remais adequate and no additional heating is required.

Termorak Oy started developing work of the ceramic spout construction spring 1981. Sunila Oy, Sunila works has been of valuable assistance to our work, from Sunila Oy we also have the longest service experiences.

The first ceramic spouts were made for Sunila Oy's T9 boiler. This boiler was choosen among other things for the reason that the spouts are very long and are so very representing for service experiences. Length of the whole spout is about 2.200 mm.

Later on have ceramic spouts also been installed in Enso-Gutzeit Oy, Kaukopää works.

The obtained service experiences have been very encouraging and after minor checking in manufactoring method as well as in material selection has the durability been extremely good.

It is well-grounded to presume that the durability in the future will be several years, particularly as compared with water cooled spouts no service risks are involved.

Termorak Oy has applied patent for ceramic smelt spout and its manufactoring method.

Due to Termorak Oy's good knowledge of recovery boiler technics we have had possibility to develop a flexible and quick spare parts service in co-operation with our customers.
This means that the customers do not need to keep smelt spouts in their own works as the spouts are available from Termorak Oy's stock at a very short delivery time.

THE INVESTIGATION AND SIGNIFICANCE OF WELD DEFECTS IN THE BOILER DRUMS

by

V.K. Lindroos, Professor of Physical Metallurgy
L.T. Suominen, Metallurgist (Dipl. Eng.)
Mexpert Consulting Engineers Ltd., Espoo, Finland

M.K. Veistinen, Metallurgist (Dipl. Eng.)
H.O. Martikainen, Metallurgist (Dipl. Eng.)
Helsinki University of Technology, Espoo, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

THE INVESTIGATION AND SIGNIFICANCE OF WELD DEFECTS IN THE BOILER DRUMS

V.K. Lindroos, Professor of Physical Metallurgy
L.T. Suominen, Metallurgist (Dipl. Eng.)
Mexpert Consulting Engineers Ltd., Espoo, Finland

M.K. Veistinen, Metallurgist (Dipl. Eng.)
H.O. Martikainen, Metallurgist (Dipl. Eng.)
Helsinki University of Technology, Espoo, Finland

1. ABSTRACT

Weld defects, which where detected by magnetic particle testing in the inner jointwelds of the boiler drums, were accordingly interpreted as weld cracks; the boiler working presently as an oil boiler has earlier been used as a black liquor recovery boiler. More detailed study of the origin and character of such defects as illustrated in this paper, indicated, however, defects to appear as slag inclusions instead of cracks, which therefore enables the further use of the boiler drums after the removal and appropriate repair welding of such defects.

2. INTRODUCTION

The safe lifetime of a construction depends predominantly on the following variables:

- service conditions (loading, temperature, etc.)
- material properties (strength, creepstrength, toughness, etc.)
- material imperfections (cracks, weld defects, inclusions, etc.)

The safe remained lifetime can be evaluated with aid of inspection procedure of a construction, such as magnetic particle testing, liquid penetrant inspection, X-ray inspection, etc.

When the size, shape and location of defects are known, the remained lifetime of a construction can be determined, provided material properties are known in service conditions. In welded constructions, such as boiler drums, imperfections are mainly located in welds, where high thermal stresses can lead to cracking. Furthermore, there are occasionally foreign inclusions, e.g. slag inclusions, in welds.

This paper presents an example of the importance of a proper choice of inspection technique when evaluating weld defects for determining the safe lifetime of a welded construction. Furthermore, there are considered the general procedure of repair welding and the necessity of post weld heat treatment in the boiler drum construction.

3. THE BACKGROUND OF THE INVESTIGATION

Weld defects were detected by magnetic particle testing in the inner jointwelds of the boiler drums. These defects were narrow shaped and about 2 - 3 mm long, which located almost in the middle of the weld perpendicular to it (figure 1). The defects were not found over 8 mm from the inner surface of the weld; the thickness of the drum wall was 40 mm.

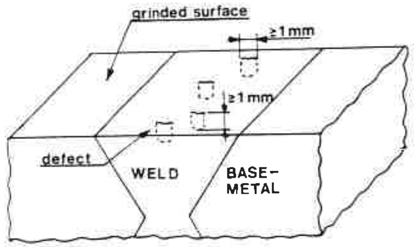


FIG.1. A schematic view of the location and size of the defects in the weld.

The boiler drums have been fabricated in the years 1948 - 1949 and the total period of use has been until now over 200 000 hours. The operating temperature of the boiler drums is 370^{o} C and operating pressure about 380 N/cm^2. Since 1960 the boiler drums were out of use for ten years; during this time they were filled up with hydratzine and they were pressure tested occasionally by 1.3-fold of operating pressure.

4. THE EXPERIMENTAL PART AND THE RESULTS

Both longitudinal and transverse samples were cut out from the inner joint weld of the boiler drum for chemical and microstructural analysis, hardness testing and defect identifications.

4.1. The material specifications

The weld metal (mark M) and parent metal (marks V and C) were analysed at The Technical Research Centre of Finland by optical emission spectroscopy; the results of the chemical analysis are presented in table 1. The parent metal is 0.26 % carbon steel and its carbon equivalent is about 0.5. The filler material is low carbon steel, which contains molybdenum; the used filler material suits well for welding the parent metal in question.

TABLE 1 The chemical analyses of the weld metal (M) and the base metal (V and C)

Sample	Composition %								
	C	Si	Mn	S	P	Cr	Ni	Mo	Cu
V	0,26	0,31	0,82	0,042	0,033	0,08	0,11	0,02	0,24
M	0,13	0,35	0,53	0,028	0,022	0,03	0,08	0,50	0,29
C	0,26	0,31	0,81	0,028	0,024	0,09	0,12	0,02	0,26

4.2. The examinations of microstructure

The transverse sample was polished and etched by nital for metallographic observations. Different weld zones and the parent metal were distinguished optically. The microstructure of the parent metal was ferritic-perlitic, where cementite of pearlite was spheroidized in the heat effected zone (HAZ) near the parent metal; also a normalized zone could be distinguished in the HAZ (figure 2). The microstructure of the HAZ near the fusion boundary was ferritic and lath martensitic; ferrite was in grain boundaries of the inherent austenite. The microstructure of the weld was of needle shaped ferrite and lath martensite (figure 2). All the observed microstructures were found typical for these type of steels.

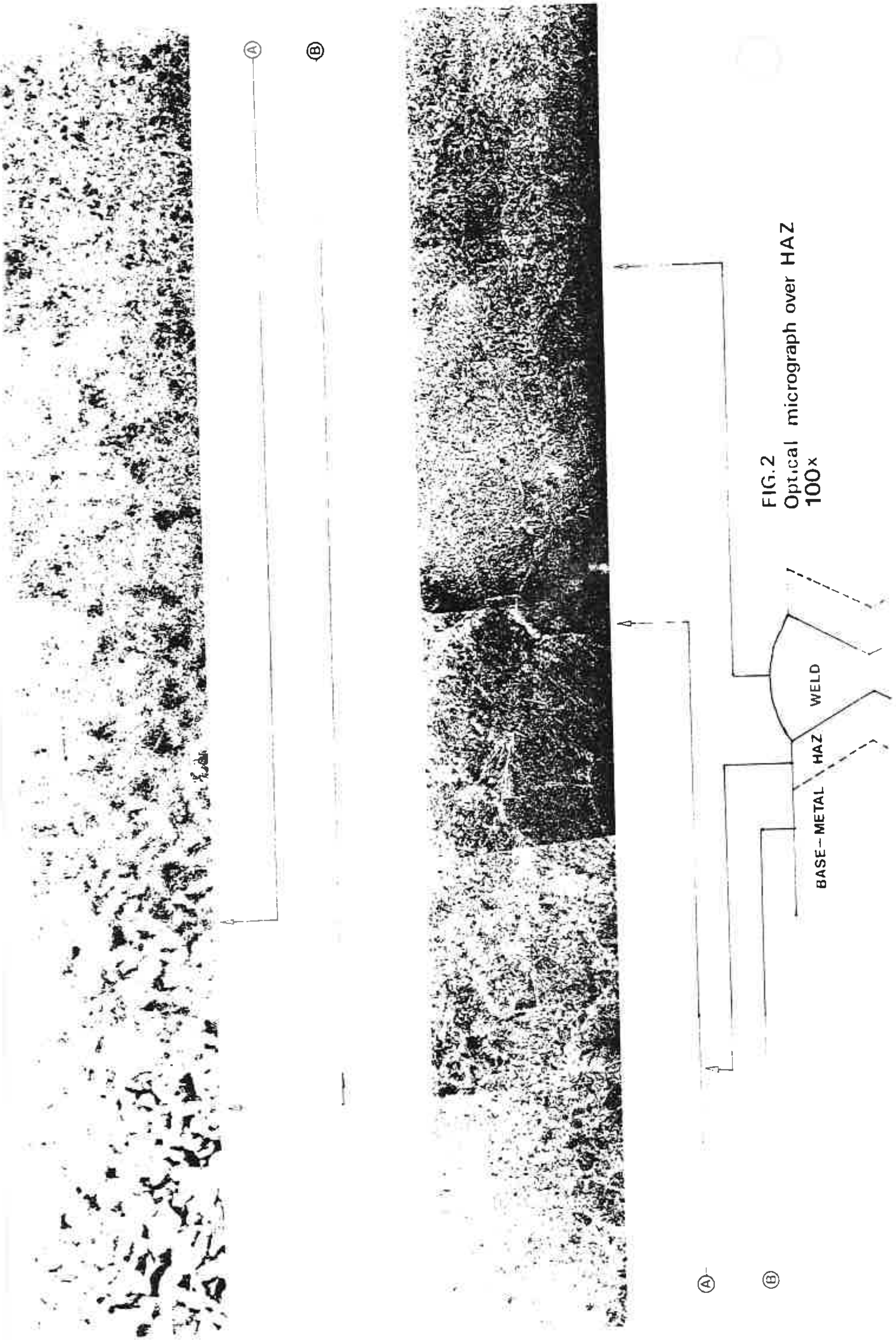


FIG.2
Optical micrograph over HAZ
100x

In the optical examination also narrow, over 1 mm long crack like defects were detected in the weld (figure 3). They seemed to contain partly the phase which resembled slag in the optical examination. The defects were all parallel, transverse to the weld and they located about in the middle of the weld(figure 1). The depths of the defects were over 1 mm and they all did not reach the surface.

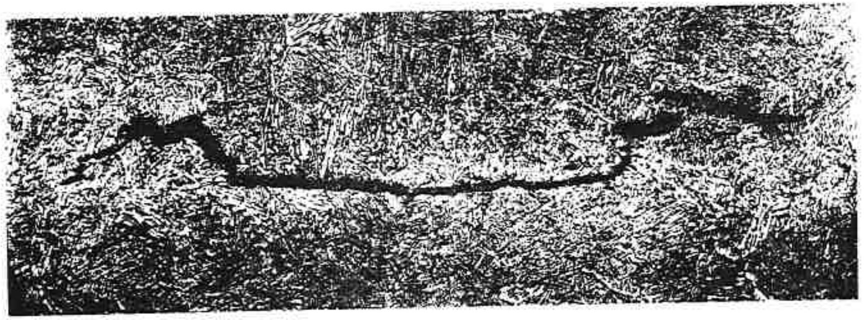


FIG. 3 Optical micrograph from a defect (50 X)

4.3. The hardness measurement

The hardness of the parent metal was about 138 HV 5 and the weld was about 30 units harder than the parent metal. Furthermore, there was a small maximum hardness in the HAZ (figure 4). The measured hardness was found typical for these type of steels.

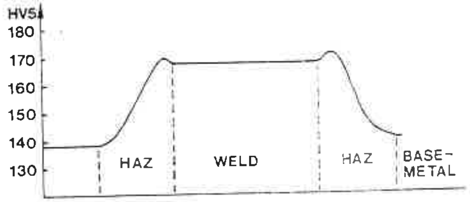


FIG. 4 The measured hardness (HV 5) over the weld

4.4. The identifications of defects

Both longitudinal and transverse samples cut out from the weld were inspected of room temperature by DIFFU-THERM-liquid penetrant inspection for locating the above mentioned defects. Some defects were detected by liquid penetrant inspection but, however, the same kind of defects as revealed by magnetic particle testing could not be detected by this technique.

Liquid penetrant inspection was done also to metallographically polished and etched surface presented in figure 3 for assuring the character of defects. Consequently, as the defects of the polished and etched surface were not detected by liquid penetrant inspection, it is evident that the defects which were, however, detected by magnetic particle testing are not cracks.

Although, the defects were narrow, their thickness was clearly over the resolution of liquid penetrant inspection by which about 0,1 mm wide and 1 mm long cracks can be detected in laboratory conditions. Even though the defects were not cracks it is, however, reasonable that they were detected by magnetic particle testing. This is because the latter technique makes it possible to detect, in ferromagnetic materials, surface and slightly subsurface linear flaws and interfaces, which separates phases of inclusions, whose magnetic properties differ from those of matrix.

On the other hand, by liquid penetrant inspection it is only possible to detect surface cracks, such as porosity and other surface connected flaws. This is because liquid penetrants operate on the basic principle, where low viscosity, low surface tension liquids will be drawn into a defect, which is open to the surface, by capillary action. By use of suitable developer a part of the penetrant is drawn from the flaw to produce a visual indication. Furthermore, it is noticeable that the indication of magnetic particle testing is a magnification of the real defect, which explains why the observed defects in polished and etched surfaces were smaller compared with the indications of magnetic particle testing. The magnification effect and the basic idea of magnetic particle testing is presented schematically in figure 5.

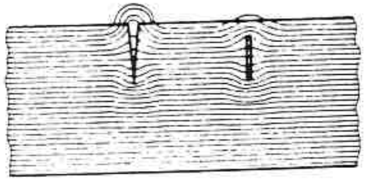


FIG. 5 A schematic view of the magnetic field effect of defects forming leakage fields at the surface

4.5. The observations of fracture surfaces

After the liquid penetrant inspection the longitudinal sample was cooled in liquid nitrogen and fractured by impact hammer. The aim of this preparation

was to result in fracture surfaces, which would contain the above mentioned defects. However, the fracture surfaces contained only pores, where surfaces were oxidized; obviously such a gas porosity has originated in welding. Because the interface between the oxidized surface and the matrix was sharp, it is evident that they have not grown during the use of the boiler drums; the gas porosity was also detected by liquid penetrant inspection.

To identify the defects detected by magnetic particle testing, the polished and etched surfaces were also studied by scanning electron microscope. By this technique it was possible to demonstrate that the crack like defects were full of slag, figure 6. Accordingly, the scanning electron microscope studies confirmed the above results of optical microscopy and liquid penetrant inspection, where the defects were indicated to be slag inclusions instead of cracks. Because the tips of slag inclusions were not open, it further confirms they have not grown during the use of the boiler drums.

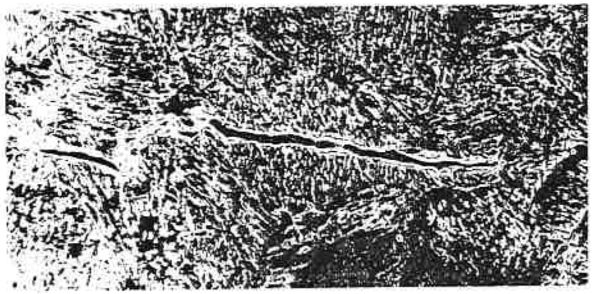


FIG. 6 SEM micrograph of the grinded and etched surface of the weld, where a defect can be seen (400 X)

5. THE WELDABILITY

In this chapter the basic factors affecting on the weldability of steels are briefly presented.

5.1. The weldability/chemical composition

The main factors influencing the weldability of steels are composition, heat input and rate of cooling. The effect of composition to weldability of carbon steels is mainly due to the carbon content. Because of increased hardenability, the steels of higher carbon contents cannot be welded satisfactorily without preheating. Other alloying elements, such as Mn, Cr, Mo, etc., which increase the hardenability, can be equalized to the effect of carbon by different formulas, which give the so-called carbon equivalent C_{eq}, equations 1 or 2:

$$C_{eq} = C + \frac{Mn}{6} + \frac{Cr+Mo+V}{5} + \frac{Ni+Cu}{15} \qquad (1)$$

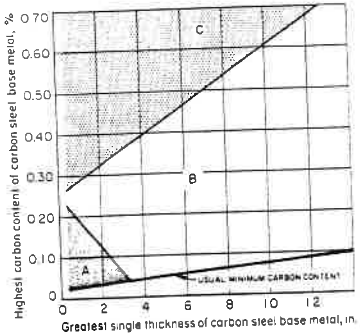
$$C_{eq} = C + \frac{Mn}{4} + \frac{Si}{4} \qquad (2)$$

where the small value of C_{eq} indicates the better weldability, and vice versa. Heat input and rate of cooling are characteristic for the welding process and technique used. These are also influenced by the dimensions of the welded sections; increasing dimensions have similar effect on the weldability as increasing carbon equivalent. The amount of martensite can therefore be kept low enough by decreasing the carbon equivalent and lowering the rate of cooling.

5.2. The postweld stresses

Suspectibility to weld cracking is due to the sum of unfavourable welding conditions; particularly due to the tensile stress, which can be formed by postweld stresses alone or in connection with operational stresses. Residual stresses can be minimized by multiple-pass welding where the first pass serves as preheat for the second pass, etc. Each filler pass also provides a postheating effect for earlier passes which causes stress relieving and tempering the martensite. Provided the effect of multiple pass welding method is not satisfactorily enough for preventing cracking, preheating as well as postweld heat treatment should be taken into consideration; preheating reduces the temperature gradient in the heat affected zone and thus lowers residual stresses.

The dimensions of the sections to be welded and the carbon equivalent of the steel whould be taken into account in the preheating as well as in the postweld stress relieving, as shown in figure 7.



A—Neither preheating nor postweld stress relieving is usually required.
B—Preheating is usually required; postweld stress relieving is not usually required.
C—Both preheating and postweld stress relieving are usually required.

FIG. 7 Combined influence of base-metal thickness and carbon content on weldability.
(Metals Handbook, Vol. 6, 8th ed.)

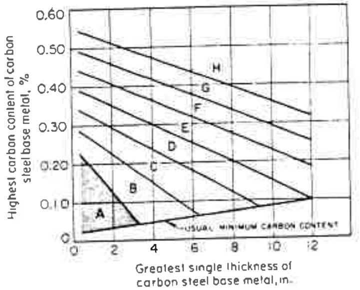
6. THE REPAIR WELDING OF THE BOILER DRUMS

In this chapter there are presented three main welding procedure variables, i.e. pretreatments of welding, welding and post-treatments of welding, which all are significant for the best result of the repair welding of the boiler drums.

6.1. Pretreatments of welding

The chemical analysis given in table 1 can be used to evaluate the carbon equivalent, where the equation 1 yields to lower carbon equivalent, C_{eq} = 0,49, than the equation 2, C_{eq} = 0,58. According to the high value of carbon equivalent, the steel used for the boiler drum material can be found difficult to weld, especially, when large sections are concerned. As it is not possible to avoid martensite formation in the heat-affected zone, it is therefore highly recommended to use preheating at the temperature 150 - 200^{0} C in order to avoid the strong susceptibility to the weld cracking. (figure 8).

Furthermore, as dissolved hydrogen is acting an agent, which makes the hardened heat affected zone brittle causing cold cracking, the shielded metal-arc welding of this kind of steel, together with low hydrogen electrodes is essential. The hydrogen can be released either from electrodes in a cellulose or from moisture provided the elctrodes are not properly dried prior to welding. The sufficient drying of electrodes can be carried out at the temperature of 300^{0} C at least one hour; alternatively the temperature of 250^{0} C at least three hours can be applied.



	Range of preheating and interpass temperatures, F	
Area	Welding with high-hydrogen electrodes(a)	Welding with low-hydrogen electrodes
A	50 to 100	50 to 100
B	100 to 200	50 to 100
C	200 to 300	100 to 200
D	250 to 400	150 to 300
E	300 to 500	200 to 400
F	350 to 600	250 to 500
G	400 to 700	300 to 600
H	450 to 800	400 to 800

(a) In practice, it is usually considered mandatory to use low-hydrogen electrodes for welding steels containing 0.50% carbon or more.

FIG. 8 Effect of base-metal carbon content and thickness on preheating and interpass temperatures for shielded metal-arc welding of carbon steel (Metals Handbook Vol. 6, 8th ed.)

6.2. The repair welding

The proper repair welding procedure consists of multiple-pass welding, starting with a small size electrodes together with the last few passes with large size electrodes. Such a repair procedure results in symmetrical residual stresses to the centre line of the weld; furthermore, stresses are small in magnitude, provided the last pass is welded in the middle of the weld bed with high heat input.

6.3. The postweld treatments

The postweld treatment can be considered useful because of high carbon equivalent and the large thickness of the welded section in question. The sufficient stress relieving temperature is 600^{0} C together with the minimum time of 2 hours. The heating and cooling of the weldment should be at a gradual rate in order to avoid thermal gradients repeatedly to result in the further residual stresses.

Consequently; the best results would be obtained when the heat treatment could be carried out in the large furnace, which is not, however, applicable for a boiler drum in a plant condition. As even the temperature 600^{0} C is complicated to arrange during repair procedure, nevertheless some improvement

will be achieved by means of continuing the preheating up to twenty-four hours. The prolonged preheating assists the dissolved hydrogen to escape and furthermore tempers the martensite in some extent. In addition, residual stresses can be partly relieved by pressurized heat treatment in connection with pressure test in operating temperature.

7. CONCLUDING REMARKS

In this paper the study of weld defects detected by magnetic particle testing in the inner jointwelds of the boiler drums was presented. By liquid penetrant inspection; optical observations and by scanning electron microscopy it was shown that the weld defects were slag inclusions instead of cracks. Furthermore, this study indicated such defects have not formed and grown during the use of the boiler drum, whereas they have originated during the construction welding of the boiler drums. Accordingly, it can be considered possible the further use of the boiler drums after the proper repair welding in which the weld bed containing defects is cut out and the seam is rewelded.

Furthermore, the general metallurgical aspects of essential importance were illustrated in order to ensure appropriate welding procedure of this type of boiler steel.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the suggestion made by Mr. Pertti Valkamo to include the present report to the symposium.

MATERIAL EVALUATION FOR BLRB SUPERHEATER TUBES

Thomas Odelstam, SANDVIK AB, Sweden, to be presented at the BLRB symposium 1982 at Helsinki.

1. Abstract

Closed-cycle systems and higher energy utilization of the flue gases, due to environmental demands and high energy prices, have led to increased flue gas corrosion on conventional superheater steels in BLRB:s.

The following measures can be taken to combat corrosion

1. Using higher alloyed conventional superheater steel,e.g. Tp T9 (9Cr, 1Mo), but the corrosion resistance is still rather poor.

2. Using austenitic stainless steel, e.g. Tp 304, 310, 321 or 347. They have good corrosion resistance, but are sensitive to possible steam side stress corrosion cracking.

3. Using composite tube with austenitic stainless steel on the outside and Cr-Mo superheater steel on the inside. Such a tube combines good resistance against flue gases with stress corrosion resistance. Various types of austenitic steels such as Tp 304, 310, 321 or 347 can be considered as the outer component. The combination Tp 310 externally and Tp T22 (2 1/4CR, 1Mo) internally is, believed to be the optimum choice.

1. Introduction

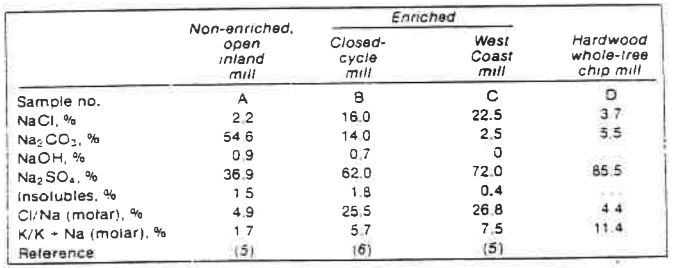
The corrosion of the superheater tubes is influenced by the following factors:

- 1. The nature of the flue gases and, thus, the type of deposits

- 2. Temperature of the tubes

- 3. Superheater tube material

Closed-cycle systems is a consequence of the stricter demands on environment protection. This in its turn has led to higher contents both of chlorides and of potassium compounds in the black liquor, a fact which is reflected especially in the form of deposits on the superheater tubes (1). Seawater-floated timber can be another source of the increased chloride levels. The deposits on the tubes mainly consist of Na_2SO_4, Na_2Co_3 and NaCl, where to a varying degree, sodium can be replaced by potassium, figure 1 beneath.



	Non-enriched, open inland mill	Enriched Closed-cycle mill	 West Coast mill	Hardwood whole-tree chip mill
Sample no.	A	B	C	D
NaCl, %	2.2	16.0	22.5	3.7
Na_2CO_3, %	54.6	14.0	2.5	5.5
NaOH, %	0.9	0.7	0	
Na_2SO_4, %	36.9	62.0	72.0	85.5
Insolubles, %	1.5	1.8	0.4	...
Cl/Na (molar), %	4.9	25.5	26.8	4.4
K/K + Na (molar), %	1.7	5.7	7.5	11.4
Reference	(5)	(6)	(5)	

Fig 1. Kraft recovery superheater deposit composition (1).

The deposits may form eutectica with a low melting point, down to approximately 520°C, if the chloride and potassium contents are high. High corrosion rates have been experienced on conventional superheater steels, e.g. T11 (1.1/4Cr, 1/2Mo) and T22 (2.1/4Cr, 1Mo) in BLRB:s where the NaCl and potassium contents were high.

As energy prices have risen, there is a trend to increase steam temperatures in the superheaters to achieve a better energy utilization of the flue gases. This also means a higher superheater tube temperature, which can reach the melting point of the deposits on the tubes and lead to high corrosion rate. A switch from water to steam cooled screen tubes has in one case caused heavy wastage of the lower

part of the superheater tubes as the temperature of these tubes i[illegible]eased. Maximum steam pressure and temperature for a welded BLRB with one dome is 10.3 MPa and 525°C resp. (2). This means that the tube temperature may reach 550°C which will increase the corrosion rates on conventional superheater steels considerably.

Finally, the corrosion rate of the superheaters depends on the tube material. This paper will evaluate different material solutions to reduce the corrosion of the superheater tubes.

3. Material tests

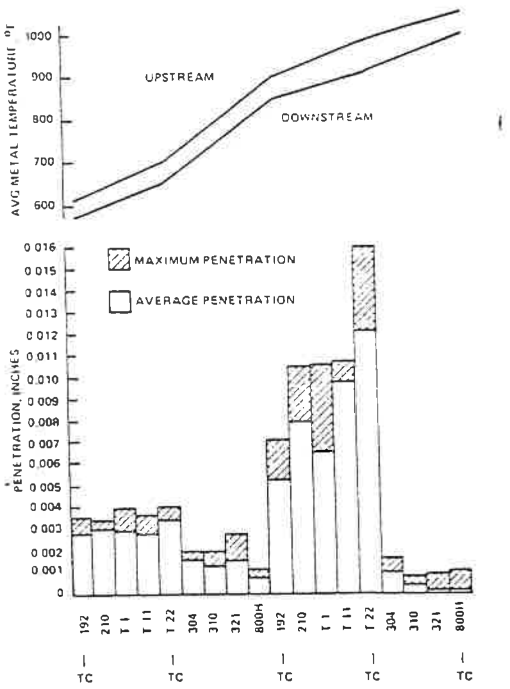
Several cases have been reported of corrosion damaged superheater tubes fabricated of 1.1/4Cr-1/2Mo and 2.1/4Cr-1Mo steels, e.g. T11 and T22. However, there are only a few trials reported where different materials have been compared in superheater environment. Perhaps the most well-known one was performed in the world's first completely closed-cycle kraft mill at Great Lakes Forest Products, Thunder Bay, (3). The following conclusions can be drawn from the trial and fig 2:

1. The corrosion resistance of low alloyed conventional superheater steels, e.g. T11 and T22, is low in closed-cycle mill and seawater transported log environment

2. Higher alloyed Cr-Mo-steels, e.g. T9 (9Cr, 1Mo), do not offer any real improved corrosion resistance

3. Austenitic stainless steels, e.g. Tp 304 (13Cr, 9Ni), 310 (25Cr, 20Ni), 321 (18Cr, 10Ni, Ti), 347 (18Cr, 10Ni, Nb) and Alloy 800H (20Cr, 30Ni) show markedly lower corrosion rates, 5-10 times, than the conventional superheater steels, but Tp 310, 347 and Alloy 800H performed best.

Other tests show results in accordance with the Great Lakes trial, fig. 3 and 4.



Second series probe: 1000 hour closed cycle operation

Fig. 2 Corrosion rates on different materials in the Thunder Bay closed-cycle mill (3)

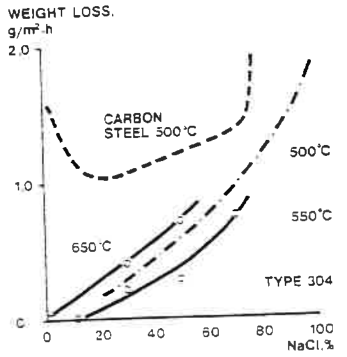


Fig. 3 Laboratory test in superheater environment with different amount of NaCl in deposits on samples. (4)

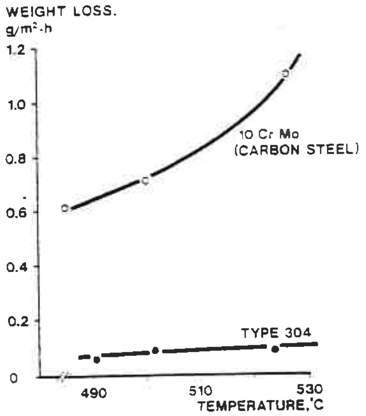


Fig. 4 Corrosion rates on carbon steel and Tp 304 in superheater mill trials for 650h. NaCl in white liquor 32-37 g/l and in deposits on samples 13 %. (4)

4. Stress corrosion cracking

Austenitic stainless steels, e.g. Tp 321 and 316 used as superheater steels in some BLRB:s have shown low corrosion rates. With such steels, however, there is a certain risk for steam side stress corrosion cracking (SCC). This risk can be considered higher in BLRB:s than in big steam power plants because of the lower superheating temperatures and more frequent transient conditions. This means increased possibility for condensation and impurity concentration on the steam side during start up and shut-down.

Reports of SCC on austenitic stainless steel superheater tubes confirm the above-mentioned risk. (6, 7, 8, 9, 10, 11)

5. Material solution for superheater tubes

Composite tubes with Cr-Mo-steel on the inside and austenitic stainless on the outside can overcome the risk of SCC on the steam side and offer high resistance against external corrosion.

Different austenitic stainless steels can be considered, e.g. Tp 304, 316, 321, 347 and 310.

Tp 347 and Tp 310 have shown the best results in trials. They can probably withstand almost all the superheater environments that can be expected. Owing to its high Ni-conent, 20 %, Tp 310 has the best resistance against general corrosion from sodium chloride and hydrogen chloride, compounds likely to be present in the future.

Thus, Tp 310 as the outer component gives a good safety margin against corrosion.

The other austenitic stainless steels will probably be resistant enough for 80-90 % of the future superheater environments. In this group Tp 304 is the best alternative due to its low price. Tp 304 is also more resistant than the stabilized Tp 321 in chloride environment. (5).

As inner component Tp T11, T22 and T9 can be considered.

The requirements on the inside component are

1. Carry the load, i.e. the max. pressure of 10.3 MPa at 525^{o}C

2. Resist stress corrosion

3. Resist steam corrosion

According to ASME Pressure Vessel Code, Section 1, Power Boilers, all three steels are allowed to be used up to 649^{o}C. But temperatures that high are not likely to occur in BLRB:s although it should be mentioned that as from 600^{o}C Tp T11 has lower allowable stress values than the others.

All three are equally resistant to SCC. T9 has the best resistance to steam corrosion owing to its high chromium content, but also T22 is considered to have quite sufficient resistance.

From a manufacturing point of view T11 and T22 are to be prefferd. .n using one of these steels in a composite tube, the heat treatments during manufacture and fabrication are easier to carry out than with the higher alloyed T9-steel.

Both with regard to strength and corrosion resistance T22 gives a wider safety margin than T11. Besides, T22, which is a well-known standard steel for superheater service, is cheaper than T9.

In summing up these viewpoints we find that the most suitable composite tube for future BLRB superheaters is Tp 310 externally and T22 internally. In less corrosive environments Tp 304 can also be considered as the outer component.

6. Fabrication of composite tubes

The fabrication technique for composite tubes is well established as a result of ten years' experience with composite tubes used as furnace tubes in BLRB:s and pulverized coal fired boilers. For instance, bending can be performed with the same methods as for conventional superheater tubes, fig 5.

7. Composite tubes Tp310/T22 for several other applications

Owing to the good corrosion resistance of the outside component, composite tubes Tp 310/T22 can also be used for instance as

1. Superheater tubes in incinerator plants where heavy corrosion can take place on low-alloyed steels because of high chloride level in the waste.

2. Waste heat boilers in synthetic gas production.

3. Pulverized coal fired boilers. Also here high corrosion rates have been experienced on low-alloyd steel, mainly due high amounts of chlorides in the flue gases (12, 13).

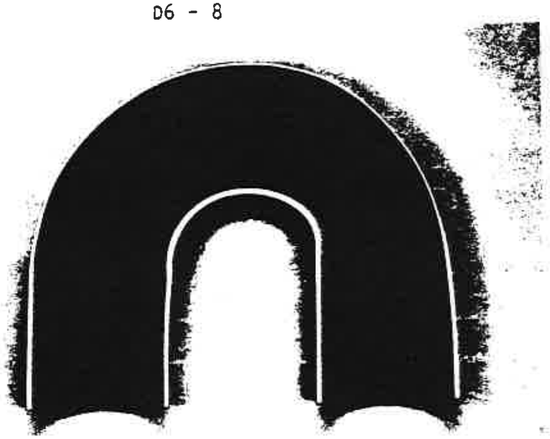


Fig 5. SANDVIK 5R10/4L7 (Tp 304/Grade Al) composite tube. Cold bending carried out to bending radius equal to the tube diameter.

8. Composite tube dimensions

In superheaters the number of different tube dimensions used is higher than for the BLRB furnace. Standardization to a few common tube sizes is therefore necessary for production reasons.

9. Conclusion

Composite tubes with an external Tp 310 component and an internal Tp T22 component is a good solution to the increasing corrosion problems with conventional superheater tubes in BLRB:s. The combination Tp 310/T22 gives high resistance against both flue gases and steam.

The same type of tube can also be used in environments similar to those in a BLRB.

References

1. D.W. Reeve, H.N. Tran and D. Barham: Superheater fireside deposits and corrosion in kraft recovery boilers. Tappi/May 1981 Vol 64, No 5.

2. T. Wahlberg: Summary of TAPPI Eng. conference 1981. Sv. pappe .dning nr 18 1981.

3. K. Morris, A.L. Plumley and W.R. Roczniak: The effect of chlorides on recovery unit superheater wastage an R & D progress report. Third international symposium on pulp and paper industry corrosion problems. May 5-8, 1980 Atlanta Georgia.

4. G. Wernquist: Trends in process technique and material choice in BLRB:s. IVL Konsult AB Report No 1054:2/76.

5. P.E. Ahlers: The influence of chloride on corrosion in the superheater of the BLRB. - a laboratory test. SSVL-report 1975.

6. A. Engl: Der Einsatz austenitischer Stähle im neuen Kraftwerk Hüls. Mitteilungen der VGB, Heft 55 August 1958.

7. W. Ruttmann und N. Brunzel: 10 Jahre austenitische Stähle im Kesselbetrieb. Mitteilungen der VGB, Heft 80 Oktober 1962.

8. V.N. Gulyaev: The use of austenitic steels in power plant units. Teploenergetika, 1971 18 (5) 67-70.

9. A. Schneider: Betriebserfahrungen und zukünftige Aussichten von Hochtemperatur - Dampferzeugern und Kraftanlagen. VGB Kraftwerkstechnik 58, Heft 3, März 1978.

10. E. Glahe, H. Jesper, G. Resch: Eindringen von Natronlauge in einen Wasser - Dampfkreislauf. VGB Kraftwerkstechnik 58, Heft 2, Febr. 1978.

11. T. Roos: Rapport från finska sodahuskommittén. The BLRB conference (sodahuskonferensen) 1981 Stockholm.

12. T. Flatley, E.P. Latham and C.W. Morris, Co extruded tubes improve resistance to fuel ash corrosion in U.K. utility boilers. Corrosion/80, march 1980, Chicago Illinois.

13. T. Flatley, E.P. Latham and C.W. Morris, Comparative performans of Superheated steam tube materials pulverized fuel fired plant environments. Conference on corrosion in coal conversion systems, London, May, 1982.

EXPERIENCES OF AUSTENITIC SUPERHEATER TUBE BENDS IN FINNISH RECOVERY BOILERS

by

P.-E. Ahlers
The Finnish Pulp and Paper Research Institute, Finland

A. Jaakkola
EKONO Oy, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

EXPERIENCES OF AUSTENITIC SUPERHEATER TUBE BENDS IN FINNISH RECOVERY BOILERS

Per-Erik Ahlers
The Finnish Pulp and Paper Research Institute, Finland

Antti Jaakkola
EKONO Oy, Finland

Abstract

Due to rapid corrosion of the lowest located tube bends in secondary and tertiary superheaters the use of austenitic materials in these bends was initiated. Now austenitic tube bends can be found in 15 Finnish recovery boilers. The first installation in which all the lowest tube bends were made from austenitic material began operation in 1973. The four recovery boilers which have been taken into operation in Finland since 1977 have all been provided with austenitic bends from the beginning.

Ultrasonic measurements and visual inspections have shown that austenitic bends have a high corrosion resistance. For kraft recovery boilers with superheated steam conditions of 480°C and 80 bar, present knowledge indicates a lifetime of at least ten years can be expected using austenitic materials as opposed to the normal three-to-five-year lifetime associated with low alloyed materials.

It would appear that austenitic material may also be well-suited to cases where high sulphur content liquor (sulphidity in smelt 97 %) is burnt. In such cases it is anticipated that most bends will achieve a lifetime in excess of ten years.

Failures of welds between austenitic and low alloyed material have not been reported.

One stress corrosion case has been reported, the failure being attributed to cloride used in acid cleaning.

troduction

A lot of corrosion problems began to appear in recovery boilers in the 1960's when higher boiler pressures and temperatures became common. In superheaters, for instance, rapid corrosion took place on the outer surface of the lowest located tube bends in the secondary and tertiary superheater to such an extent that some bends had to be replaced after two or three years.

It was known that austenitic stainless steel has in general a better corrosion resistance than carbon and low alloyed steels, and in the early 1960's the first installation of austenitic bends were made in Rauma-Repola Oy's CE-recovery boiler (sodium sulphite process).

More systematic studies of the corrosion resistance of different metals were started in Finland and Sweden. Laboratory investigations indicated that austenitic stainless steel has a very high corrosion resistance in superheater flue gas conditions (1). Field tests made with air cooled probes in the superheater zone confirmed the superiority of the austenitic materials tested (2). This is shown in Fig. 1.

Worn-out bends of conventional material began to be gradually replaced with homogenous austenitic bends in secondary and tertiary superheaters in the mid 1970's. Since 1977 four new recovery boilers have been taken into operation in Finland. In these boilers all the lowest bends are of austenitic material in the secondary and tertiary superheaters.

As shown in Table 1, austenitic bends currently are used in 15 of the total 29 recovery boilers running in Finland. In ten boilers all the lowest bends in the secondary and tertiary superheaters are of austenitic material. In three boilers a significant number of bends are of this material. Two boilers have only a few austenitic bends.

Austenitic materials

Table 2 gives the nominal analyses of the stainless steel grades used. Most of the bends are of AISI 347, AISI 304 and AISI 321 grades. Recently a couple of bends of AISI 316 have been installed in a boiler.

The weld metal must be overalloyed to assure optimal microstructure and to keep a high chromium content in the final weld. In most cases weld metal containing molybdenum (AISI 309Mo) is used to provide a strong bond between the austenitic and low alloyed steels.

The cold bended seamless stainless steel tubes are joined to the superheater tubes by multipass welding using TIG (Tungsten Inert Gas) or MMA (Manual Metal Arc) methods . To get a perfect joint in mill conditions it is common to fit short tubes of the superheater material by welding them under controlled conditions in the workshop. To avoid embrittlement the stainless steel being joined by welding to carbon or low alloyed steel is usually preheated before welding. No other heat treatment is needed.

Practical Experiences

All boilers in Table 1 except No 1 are normal kraft recovery boilers, most of them operating with a boiler pressure of 80 bar and a superheated steam temperature of 480^{o}C. White liquor sulphidity varies from 28 to 40 per cent.

In general, the austenitic bends have been checked annually, using both visual inspection and ultrasonic wall thickness measurements. Results obtained in the kraft boilers show that the corrosion rate has been very low. There is a considerable scattering in the data obtained due to commonly experienced practical difficulties in obtaining reproduceable values from field measurements. However, it can be stated that the corrosion rate of the austenitic bends in most cases has been around 0,1 mm/a, and thus substantially lower than the rates of 0,3 - 0,6 mm/a obtained for conventional materials. No significant differences have been found between the various austenitic steel qualities in use. So far only a few austenitic bends have had to be replaced in the kraft boilers due to gas side corrosion. In addition, inside stress corrosion has damaged some bends in the boiler No 2. This case is discussed later in more detail.

Boiler No 1 is a sodium sulphite recovery boiler. Corrosion conditions are exeptionally heavy because of the extremely high sulphur content in the liquor (sulphidity in smelt 97 %). This boiler was built in 1973 with all the lowest bends of austenitic material. The corrosion rate has been on the average quite moderate, about 0,12 - 0,14 mm/a, however, there has been locally a more rapid corrosion on one side, where rates of 0,4 - 0,5 mm/a have been found. Nevertheless, after nine years operation only about 20 per cent of the original bends have been replaced. There have been replacements both in secondary and tertiary superheaters.

Discussion

The high corrosion resistance of austenitic material in hot flue gas conditions is associated with some specific properties of chromium oxide, that is the protective coat formed on the metal, and its good stability at high temperatures.

From both the theoretical and practical point of view it is known that a passivity can be broken down at a high temperature in an atmosphere with a high sulphur content. In reducing furnace conditions, 500^{o}C has been found to be the threshold temperature above which, corrosion takes place (1). On the other hand it has been found that in oxidizing superheater conditions no corrosion occured even at 650^{o}C (2). It can be concluded that with normal kraft sulphidity the safe upper limit is much higher than the normal operating temperature. It is further apparent from figure 1 that for stainless steels, the temperature range studies - 490^{o}C to 525^{o}C - must lie completely below the critical limit, since there is no real evidence of any temperature effect on the corrosion rate.

The effect of metal composition on corrosion has unfortunately not been studied as systematicly in superheater conditions as in furnace conditions (3). Results obtained in laboratory and field tests (1, 2) indicate, however, that the composition is not very critical provided that the chromium content is high enough. Twelve per cent is the threshold value in the furnace conditions and apparently in superheater conditions as well as indicated by the results in Fig. 2.

Stainless steels endure well in conditions that normally prevail on the steam side of tubes. However, cracking of tube walls is possible under certain conditions as was indicated earlier.

This superheater failure occured rather soon after the start up. Reparations in the lower part of the unit were subsequently acid cleaned with a solution containing hydrogen chloride.

As shown in Fig. 3 the cracks have started from the inside. Fig. 4 shows that the cracking has occured about 20 mm below the weldseam. Branched cracks propagated through grains in a mode typical for stress corrosion caused by chloride or alkali as shown in Figure 5. None of these chemicals were found on the fracture surface or in the vicinity. It is possible that during leakage, steam swept the chemicals away.

No sensitizing of the material had occured, but in the metal near the inner surface, strain lines were found indicating that plastic straining had occured. Such lines were absent in the middle and in the outer part of the wall. During start up a significant temperature gradient through the tube wall can be built up, particularly if tubes are partly filled with water, and consequently tension stresses appear on the inner side of the wall. A temperature difference of 100°C produces stress levels high enough for cracking to start. Once triggered the cracks propagate at a high velocity (on the order of 10^{-8} -10^{-7} m/s (4), and a total failure can occur, as in fact happened in this case in less than two hours.

The failure was related to stress corrosion cracking caused by chloride, that, despite ordinary precautions in the cleaning procedure, evidently found its way to the superheater. Small amounts are sufficient to initiate the cracking.

clusion

Austenitic bends have shown in service a high corrosion resistance, and on the basis of the field experiences, a lifetime of over ten years in kraft and about ten years in sulphite recovery boilers can be expected.

On the average the use of austenitic material results in a lifetime at least five times longer than can be obtained with carbon or low alloyed steels. The composition of the austenitic material does not seem to be very critical. Weld joint between dissimilar metals have not been the source of any problems.

It should, however, be noted that stainless steel's susceptibility to stress corrosion cracking necessitates care in operating and maintenance procedures.

REFERENCIES

1. Moberg, O., International Seminar of Pulp and Paper Industry Corrosion Problems, Vol. 1, National Association of Corrosion Engineers, Houston, 1974
2. Ahlers, P-E., Progress report of 28 of the SSVL project 7, Stokcholm, 1976
3. Ahlers, P-E., 7'th Scandinavian Corrosion Congress, Trondheim, 1975, pp. 580-590
4. Wendel-Kalsch,E., Werkstoffe und Korrosion 29 (1978), p. 708

Table 1. Boiler installations in Finland where the lowest tube bends in the superheater are made of austenitic material (August 1982)

No.	Boiler mfr. 1)	Year of commissioning	Nominal dry solids burning capacity t DS/d	Superheated steam		White liquor sulphidity	Austenitic lowest superheater bends			
				Pressure bar	Temperature ^oC	%	Installation started Year	Superheater location	Extent of installation %	Material cod
1	T	1973	1050	65	460	97 2)	1973	Sec.+Tert.	100	AISI 304
2	CE	1959	690	80	480	32	1975	Sec.	100	AISI 347
3	AW	1961	460	80	480	38	1975	Tert.	<10	AISI 347
4	GV	1965	750	80	480	31	1976	Sec.	50	AISI 347
5	AW	1977	1500	80	480	40	1977	Sec.+Tert.	100	AISI 347
6	T	1977	1250	80	480	35	1977	Sec.+Tert.	100	AISI 347 3)
7	GV	1977	1300	80	480	30	1977	Sec.	100	AISI 304 L
8	AW	1975	1300	80	480	35	1979	Sec.+Tert.	100	AISI 347
9	T	1964	750	80	480	31	1980	Tert.	100	AISI 347
10	AW	1967	420	80	480	32	1980	Tert.	30	AISI 321
11	AW	1980	650	65	480	34	1980	Sec.+Tert.	100	AISI 304
12	AW	1971	410	80	480	35	1980	Tert.	80	AISI 304
13	AW	1962	700	80	480	28	1981	Tert.	100	AISI 321
14	CE	1961	730	80	470	30	1982	Sec.	100	AISI 304
15	CE	1964	640	80	480	35	1982	Tert.	<10	AISI 304 L

1) AW A. Ahlström
BW Babcock & Wilcox
CE Combustion Engineering
GV Götaverken
T Tampella

2) Sodium sulphite process

3) Some test bends of AISI 316

Table 2

Nominal analysis (wt%) of austenitic bends and weld metals

Alloy	C_{max}	Cr	Ni	Mo	Other
Tube Metal					
AISI SIS					
304 2333	0,05	18	9		
304L 2352	0,03	18	10		
321 2337	0,08	18	10		Ti 5xC
347 2338	0,06	18	10		Nb 10xC
316 2343	0,05	17	12	2,7	
Weld Metal					
AISI					
(309)	0,05	23	14		
(309Mo)	0,05	22	15	2,6	

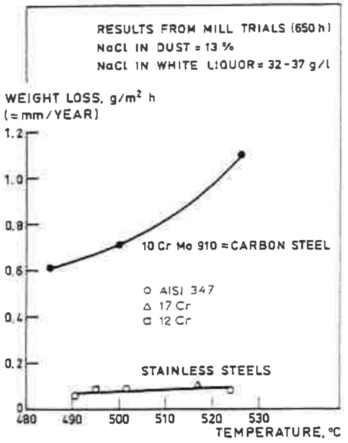


Fig. 1.
Field test results of the effect of temperature on corrosion rate (2).

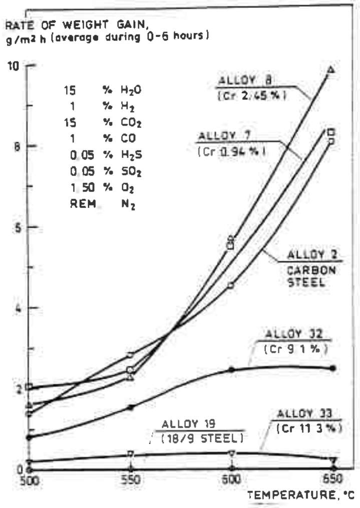


Fig. 2.
Laboratory results of the effect of temperature on corrosion rate (1).

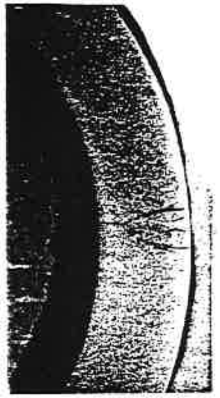


Fig. 3.

Cross section of the damaged austenitic tube. The cracks have propagated from inside out.

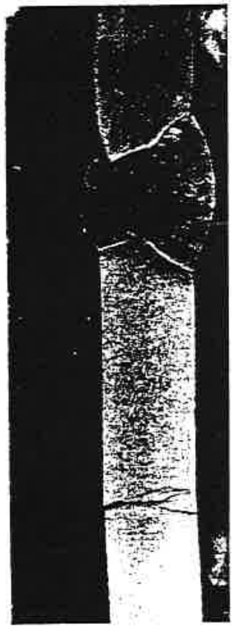


Fig. 4.

Longitudinal section of the tube wall in the vicinity of the weld. Cracks in the austenitic material.

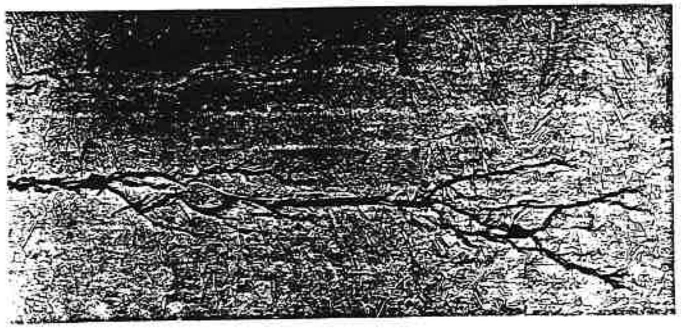


Fig. 5.

Close up of Fig.3 showing transgranular cracks. 200X

COMPOSITE TUBES IN RECOVERY BOILER FURNACES
A SUMMARY OF TEN YEAR'S EXPERIENCE IN SWEDEN

by

S. Ingevald
F. Bruno
Industrins Processkonsult AB - IPK, Sweden

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 - September 1, 1982

COMPOSITE TUBES IN RECOVERY BOILER FURNACES
A SUMMARY OF TEN YEAR'S EXPERIENCE IN SWEDEN

Sture Ingevald,
Fredrik Bruno

INDUSTRINS PROCESSKONSULT AB - IPK, Sweden

1. Abstract

Composite tubes have been used in the lower furnace of Swedish Recovery boilers for ten years. Today we have in total 11 boilers which are equipped with composite tubes in the furnace. Six of these are old boilers where the lower part of the furnace walls have been replaced either completely during one shutdown or successively tube by tube during regular maintenance stops. There are also some boilers on which only some of the tubes have been substituted.

The experiences until now are positive and only minor corrosion and a few damages have been reported. Most of the faults reported refer to improper original design. Some further design improvements may be possible.

One can expect that the lifetime of a furnace with composite tubes will be 20 years or more. Our experience until now indicates that the need for maintenance work will be much less than on earlier wall designs.

2. Background

Recovery Boilers of the Tomlinson type have been in use for about 50 years. Until the late 1950's the furnace tubes on all Swedish Recovery Boilers were protected by Bailey-blocks on the fire side. On the boiler sizes asked for at that time these cast iron blocks gave a too heavy structure and the tangential tube wall was introduced. On some of these boilers the furnace wall carbon steel tubes were completely unprotected. After a few years in operation it become evident that unprotected tubes in high pressure recovery boilers suffered from severe corrosion on the flue gas side, with corrosion rates sometimes exceeding 0.5 mm/year.

Different methods have since then been used to protect and maintain furnace wall tubes. The most common are:
- Metallizing
- Cladding
- Studding

At least on Recovery Boilers which suffer from high corrosion rates none of these methods gives an acceptable lifetime to the tubes. On some boilers a renewal of the lower furnace or parts of it has been necessary to perform within 5-10 years.

During the period 1964-72 extensive investigations were made about this type of corrosion and how to prevent it within a Swedish-Finnish co-project. This investigation showed among others that corrosion on carbon steel under actual conditions increases with the temperature of the material, especially above 300°C. This has restricted the working pressure to below 6.5 MPa. The corrosion resistance of the stainless quality AISI-304 (i.e. corresponding to our SIS 2333 quality) was found to be very good up to about 500°C.

The Swedish steel mill SANDVIK, which since many years has made coextruded tubes for components in nuclear installations, now introduced a composite tube with an outside layer of type 304 stainless steel. Test panels with SANDVIK composite tubes were first installed in 1967 in a Recovery Boiler at the Kaukopää mill in Finland.

When AB Statens Skogsindustrier (ASSI) planned for a new Recovery Boiler at their Lövholmen mill in north Sweden, Messieurs Bertil Fagerlund et al decided to choose composite tubes for the walls in the lower furnace. After careful investigations, in cooperation with the Swedish Steam Users' Association and the manufacturer OY Tampella AB, ASSI specified a membrane wall design with composite tubes Ø 63.5 x 7.25 mm and carbon steel fins 12,7 x 4.0 mm. The tubes have an outer layer (1.65 mm) of stainless steel AISI 304 on a base material (5,60 mm) of conventional carbon steel. ASTM A 210 Grade A1. This is today the standard material combination in SANDVIK composite tubes for Recovery Boiler water walls.

Being the first Recovery Boiler with a complete lower furnace of composite tubes the Lövholmen boiler was started up in April 1972. In the meantime the nearby SCA mill at Munksund in 1971 started to change, successively, wall tubes in their at that time ten years old boiler. Ten years later they had composite tubes all around the walls.

In table I below are noted the main data from Recovery Boiler originally buildt with composite tubes.

Table I - RECOVERY BOILERS WITH COMPOSITE TUBES

	Capacity D.S./24h Tons	Design Pressure MPa	Outlet steam Press MPa	Outlet steam Temp °C	Wall panel design	Height of composite tubes m	Start up Year	Boiler* manufacturer
1. ASSI, Lövholmens Bruk	600	6,7	6,0	480	Carbon steel fins 17,5 x 4,0 mm	6	1972	Ta
2. MoDoCell AB, Husum	1815	7,5	3,8	450	Tangential	9,5	1978	GVÅ
3. Södra Skogsägarna AB, Mönsterås Bruk	1600	7,6	6,2	460	"	9	1979	GVÅ
4. ASSI, Karlsborgs Bruk	1250	7,5	6,3	450	"	9	1980	GVÅ
5. Svenska Cellulosa AB Ostrands Bruk	1500	7,6	6,1	450	"	9	1982	GVÅ

* Ta - OY Tampella AB Finland; GVÅ - Götaverken Ångteknik AB

On a number of boilers, listed in Table II, a complete changing to composite tubes in lower furnace or local repairs have been made. Two of the boilers (No 5 and 6) were originally equipped with Bailey Blocks. On these each tube now is replace by two composite tubes, thus giving tangential tube walls in the renewed lower furnace.

Table II - RECOVERY BOILERS REPARIED WITH COMPOSITE TUBES

	Boiler	Capacity D.S./24h MPa	Design Press MPa	Steam Press MPa	Steam Temp °C	Wall* Design	Height of composite tubes m	Start up Year	Composites Installed	Manufacturer	Notes
1. SCA, Munksund		600	6,7	6,0	480	T	4,5	1965	1971-80	GVÅ	
2. MoDoCell, Husum	TP7	700	7,4	6,0	480	T	10	1965	1980	GVÅ	
3. Kopparfors, Norrsundet	SP65	460	6,7	5,8	450	T	5,5	1963	1979	SMV/GVÅ	
4. Kopparfors, Norrsundet	SP70	560	6,6	5,8	450	M	-	1970		GVÅ	Smelt Spouts
5. MoDoCell, Alfredshem	P8	490	4,1	3,6	445	T	10,5	1958	1981	GVÅ	
6. ASSI, Frövifors	P03	725	7,5	4,0	450	T	9,5	1967	1980	GVÅ	
7. Södra Skogsägarna, Värö		1400	7,5	5,8	450	M	-	1972	1979	GVÅ	Smelt Spouts
8. Billerud, Skoghallsverken		675	5,5		450			1969	1981-82	SMV/GVÅ	Front & Side walls

* T = Tangential; M = Membrane

As can be found from table II there are five boilers on which the lower furnace has been completely changed and equipped with composite tube walls. As an example may be mentioned that the furnace at Norrsundet (NO3) was exchanged during a total downtime of only 28 days.

3. Experiences from construction and repairs

No serious problems have been reported from the prefabrication and erection of composite tube walls. The designs, welding and other manufacturing procedures seem thus to have been well investigated.

There are, however, a few damages which may be related to an improper design.

Figure 1 illustrates the shape of one of the smelt spout openings on the Lövholmen Tampella boiler after one year of operation.

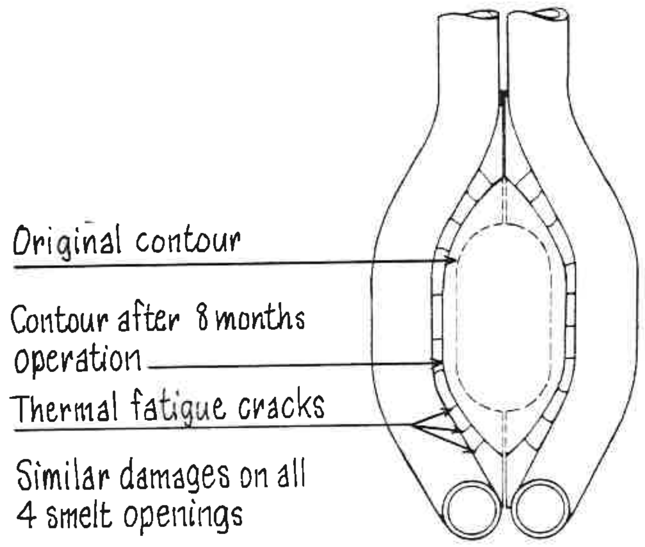


Fig. 1. Smelt spout opening

As the figure show the stainless steel fins are heavily burned back and cracked. Some of the cracks, which were of the thermal fatigue type, had penetrated into the tubes. At a following close examination of the tubes some minor (micro-) cracks were found at welds for stud pins. New smelt spout tubes without these wide fins and without studs were installed and have since then worked without any problems.

Also Götaverken's original design of smelt spout openings with composite tubes has suffered from problem with cracking.

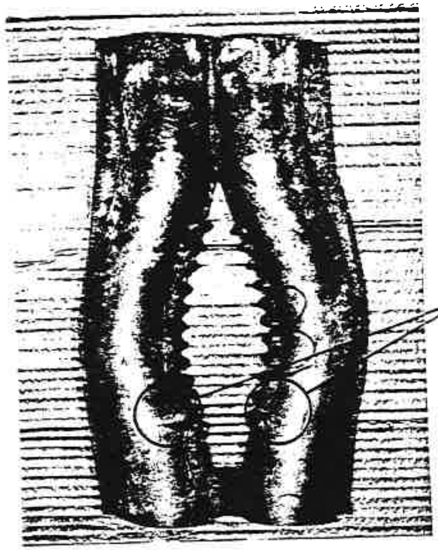


Fig. 2
GVÅ smelt spout opening

On the tubes surrounding the opening small stainless round bars are welded - Fig. 2. These are aimed to protect the tubes from careless rodding. Already within a year of operation cracks have appeared at these bars and penetrated through the stainless layers. Fig. 3.

Fig. 3
Detail from fig. 2

Fig. 4
Cross secion of
smelt opening
tube. 7x

Fig. 4 above shows a cross section of a tube with welded on round bar. As this figure shows no one of the cracks penetrate the carbon base material.

Above mentioned damages show that heat transformer fins and studs should be avoided.

On a boiler which had been in operation for about one year the stainless layer had locally spalled as can be seen on the photo in Fig. 5.

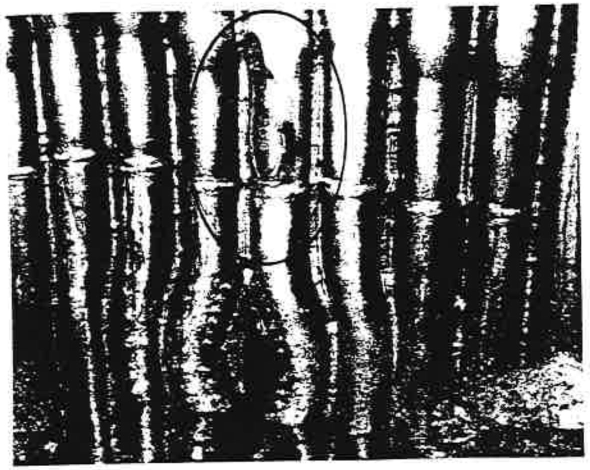


Fig.5
Local spalling of
the stainless layer

Also this damage has been considered as caused by a manufacturing fault. Most probably there has been an incomplete bonding which has passed the 100% ultrasonic test that all composite tubes pass. This bond defect may have become worser when the actual tube diameter was reduced at the boilermanufacturer. Due to the bond defect the stainless layers have been overheated during normal operation and then cracked and spalled of (figure 6).

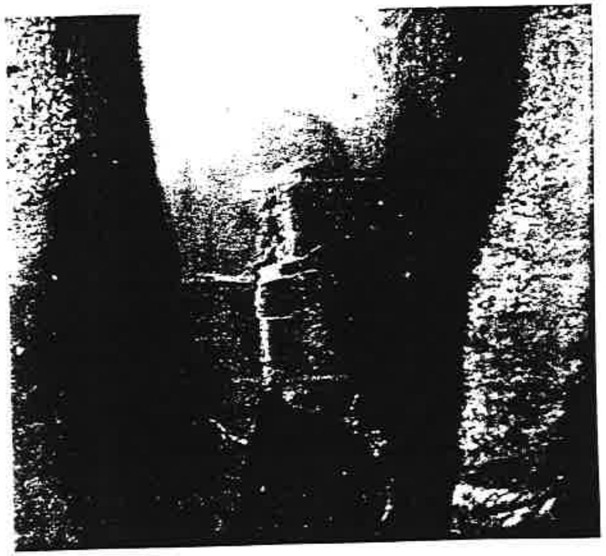


Fig. 6
Detail of fig. 5

This type of defects seems to be uncommon and we do not consider them as serious because they are easy to detect at regular inspections.

4. Faults caused during operation

Also faults which could be related to operational conditions are few. In one case cracks have been found in the stainless layers on tubes surrounding a smelt spout opening. The cracks are of the stress corrosion type, see Fig. 7.

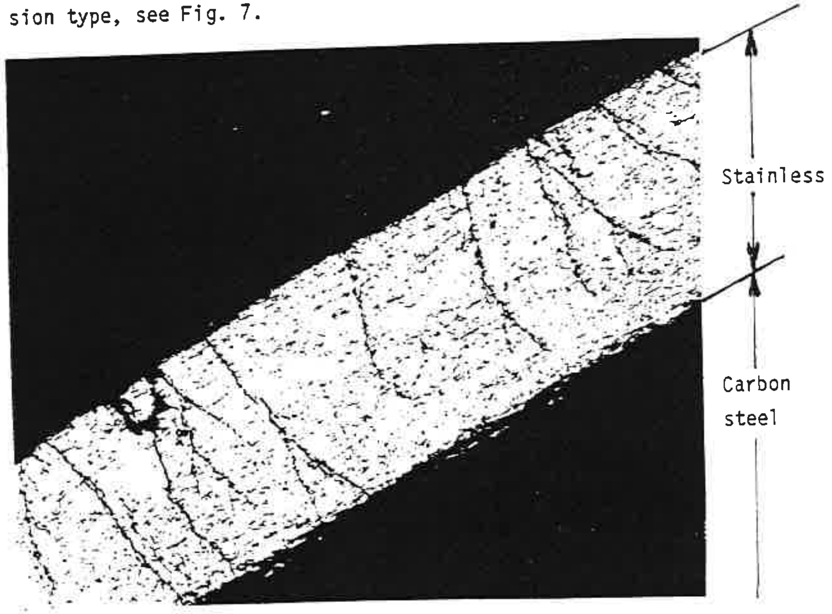


Fig. 7. Stress corrosion cracks

The real cause is until now not known, but no cracks have been found at the corresponding tube areas on other boilers. Thus we consider that there are extremely unfavourable conditions at the cracked area in this boiler. In the vicinity of the cracked area there was also a thinned area. The stainless layer had locally decreased with about 0,5 mm in one year.

We recommend that tube areas which like these are exposed to flowing smelt are carefully inspected and regularly measured with regard to thickness. The use of a fine grained abrasive and a magnifier glass may be helpful, as these type of stress corrission cracks are very tight and hard to detect (see fig. 7)

One advantage is that composite tube walls as a rule are comparatively easy to clean for inspection. At visual inspections local tendencies to surface corrosion have been noted through variations in the colour and the surface structure. Measurements made have in these cases not indicated any measurable decrease of the tube thicknesses.

5. Summary and conclusions

The first Recovery Boiler with composite tubes has now been in use for ten years. The experience from this, as well as from boilers which have operated for a shorter time, indicates that a lifetime of twenty years or more for a composite tube furnace seems realistic without extensive maintenance work.

As the number of boilers with composite tube furnace increases one can expect that new problems will occur. It must be kept in mind that many of the new boilers operate under more extreme conditions. The steam-pressure tend to be higher as the dry content of the liquor. Also the conditions of the smelt may change e.g. through higher chloride content.

Thus, also in the future inspectors must watch carefully on every sign of corrosion, cracks or other faults, that can result in a tube leak. Special attention shall be paid to all surfaces in direct contact with flowing smelt.

Designers must pay more attention to the smelt outlets. Here as elsewhere plates, rods or pin studs welded to the tubes should be avoided if they result in high local heat transfer.

It must also be recommended that maintenance departments and manufacturers work out routines, welding procedures etc. for repairs on composite tube walls. It must be possible to make a local repair of the stainless layer in the future, and to avoid extra downtime when an unforeseen incident occurs.

COMPOSITE TUBES IN RECOVERY BOILER FURNACES
A SUMMARY OF TEN YEARS' EXPERIENCE IN FINLAND

by T. Roos, EKONO Oy, Helsinki, Finland

Paper to be presented at the

Black Liquor Recovery Boiler Symposium 1982, Helsinki, August 31 -
September 1, 1982

D8 - 1

COMPOSITE TUBES IN RECOVERY BOILER FURNACES
A SUMMARY OF TEN YEARS' EXPERIENCE IN FINLAND

T. Roos, EKONO Oy, Helsinki, Finland

In Finland today the use of composite tubing is the dominent method of protection against furnace corrosion. Nineteen of the thirty working recovery boilers are equipped with composite tubing.

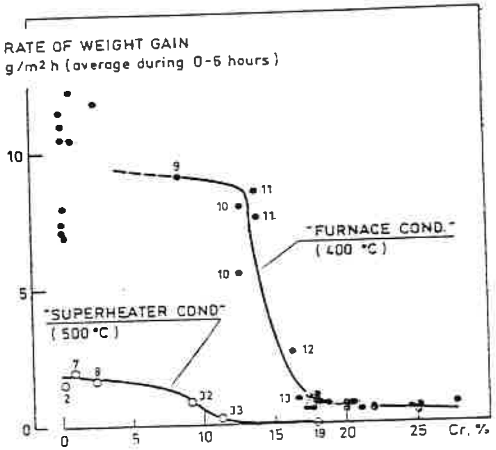
Joint Swedish-Finnish investigations in 1964 - 72 indicated clearly that AISI 304 has a very high resistance against recovery boiler corrosion in both furnace and superheater conditions. Some of the laboratory results (under test conditions listed in Table 1) are presented in figures 1 and 2.

Table 1

Laboratory Test Conditions

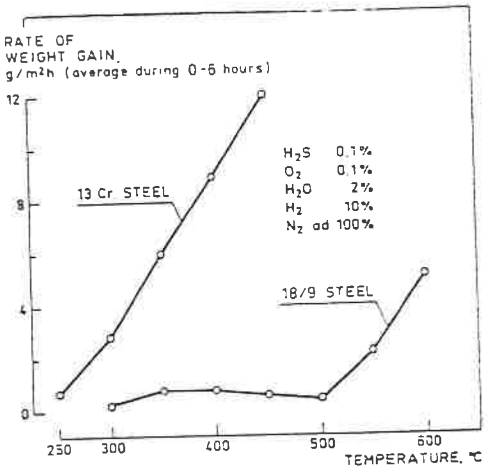
		Furnace	Superheater
Temperature	$^{\circ}$C	400	500
H_2S	%	0,1	0,05
SO_2	%	-	0,05
O_2	%	0,1	1,5
H_2O	%	15	2
H_2	%	10	1
CO_2	%	10	15
CO	%	-	1
N_2		Remainder	Remainder

Fig. 1



Effect of chromium content on corrosion rate under furnace condition and superheater condition.

Fig. 2



Effect of temperature on the weight gain rate for 13Cr and 18Cr-9Ni steel at furnace conditions.

Table 2 shors the main data for recovery boilers equipped with composite tubing.

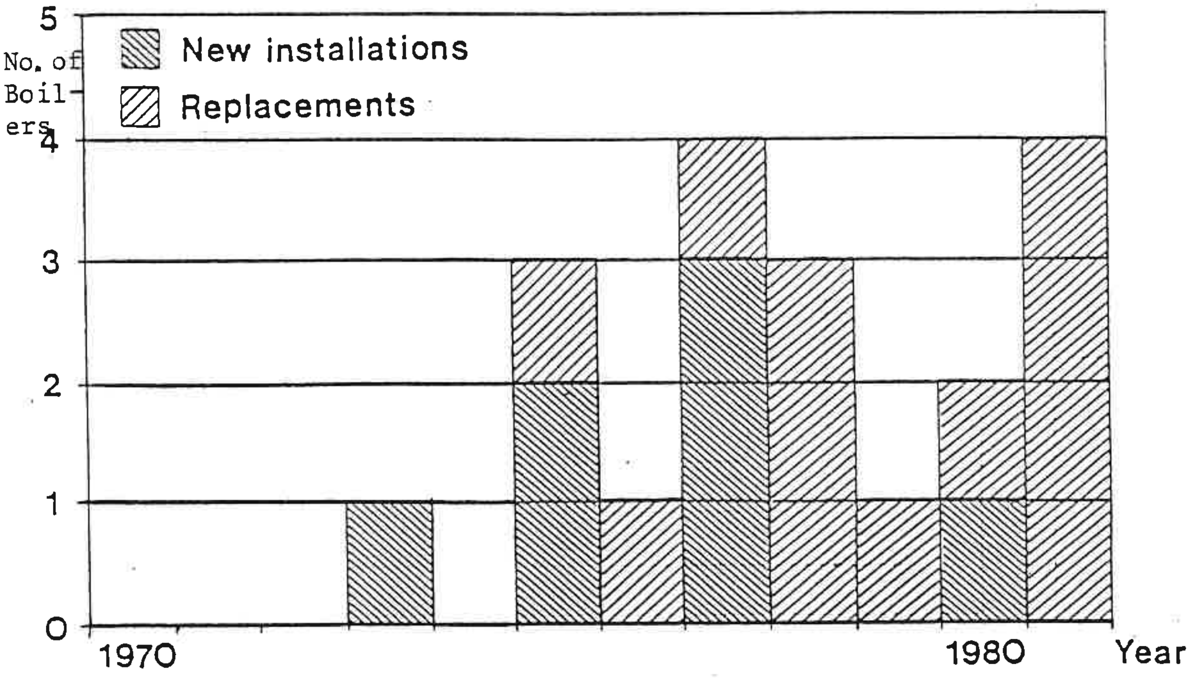
Table 2 - Recovery Boilers with Composite Tubes

Boiler	Capacity TDS/day	Drum Pressure MPa	Composite Tubes Installed Floor/Walls m/Year (Height)
Rauma-Repola Tampella	1050	7	- / 5+9,5 / 1973
Schauman Ahlström	1500	9	+ / 8,6 / 1975
Tervasaari Tampella	1000	9	+ / 5,5 / 1975
Kemijärvi Tampella	750	9	+ / 5,5 / 1975
Schauman Ahlström (BW)	800	7	+ / 7 / 1976
Kymi Götaverken	1300	9	- / 8 / 1976
Metsäbotnia Ahlström	1500	9	+ / 9,8 / 1977
Veitsiluoto Tampella	1250	9	- / 8 / 1977
Kymi Götaverken	520	9	- / 8 / 1977
Kemi Götaverken	1080	9	- / 15 / 1978
Oulu Götaverken	750	9	- / 9 / 1978
Sunila Tampella	580	7	- / 5,5 / 1978
Heinola Tampella	140	9	- / 4,5 / 1979
Uimaharju Ahlström	420	9	+ / 8,8 / 1980
Varkaus Ahlström	600	7	+ / 4 / 1980

Boiler	Capacity TDS/day	Drum Pressure MPa	Composite Tubes Installed Floor/Walls m/Year (Height)
Joutseno Ahlström	580	9	- / 3 / 1981
Tainionkoski Ahlström	730	9	- / 14,1 / 1981
Kaukas Ahlström	410	9	+ / 8,9 / 1981
Kotka Ahlström, CE	680	9	+ / 11 / 1981
Joutseno BW	400	7	- / 3 / 1983

Comparing the data in Table 2 with corresponding data from Sweden, the only notable difference is that the average pressure level is higher in Finland (9 MPa in Finland - 7 MPa in Sweden). In Figure 3 the year and degree, to which installations and replacements using composite tubing have been made in Finland, is presented.

Figure 3



Until now no serious problems have been reported. Only a few cases of damage have been noted, those being due to small cracks related to welded joints.