

Institute of Paper Science and Technology Atlanta, Georgia

IPST Technical Paper Series Number 710

Corrosivity Monitoring Database for Kraft Recovery Boilers

G.J. Fonder, S.J. Al-Hassan, and P.M. Singh

March 1998

Submitted to 9th International Symposium on Corrosion in the Pulp and Paper Industry Ottawa, Ontario, Canada May 26–29, 1998

Copyright[©] 1998 by the Institute of Paper Science and Technology

For Members Only

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and
- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and
- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

The Institute of Paper Science and Technology assures equal opportunity to all qualified persons without regard to race, color, religion, sex, national origin, age, disability, marital status, or Vietnam era veterans status in the admission to, participation in, treatment of, or employment in the programs and activities which the Institute operates.

CORROSIVITY MONITORING DATABASE FOR KRAFT RECOVERY BOILERS

Gregory J. Fonder, Safaa Al-Hassan, and Preet M. Singh

Institute of Paper Science and Technology Atlanta, GA 30318

ABSTRACT

A database containing corrosion-related information for recovery boilers was developed based on published data critically reviewed and extracted following an extensive literature survey. The database can be used either to aid in material selection for a particular environment or to predict the behavior of a material in a variety of environments. The results of a search may be viewed on-screen, printed, or exported to a spreadsheet for further manipulation or presentation in graphical format.

INTRODUCTION

Fireside corrosion of kraft recovery boilers is a continuing problem in the pulp and paper industry. Excessive corrosion causes water-wall thinning and can lead to tube leakage or rupture. This can then lead to smelt-water explosions that cause equipment damage and injuries to mill personnel. The corrosion mechanism in the lower furnace area is believed to be sulfidation. However, other industries, including petroleum, chemical, and electrical power generation, have experienced sulfidation in the past and have conducted research in this area. Some data on the corrosion behavior of materials used in kraft recovery boilers has been generated at IPST, PPRIC, the Swedish Corrosion Institute, and a few other research groups. [1-4]

A detailed survey of the available literature concerning the oxidation and/or sulfidation of various steels, nickel-base alloys, and component metals relevant to recovery boilers was conducted. The articles collected were critically reviewed and any relevant data were extracted for use in the database. The data included is divided into three main categories: isothermal, cyclic temperature, and cyclic gas with or without cyclic temperature. The database includes experimental results on the effect of smelt on the corrosion rate. A strict procedure was followed to ensure that the numerical values entered into the database were accurate and that all data were entered into the appropriate record.

The database contains data collected from 200 references and is fully searchable. These references contained a large amount of data on many materials, gas environments, and smelts applicable to recovery boilers. The desired temperature range for data to be entered into the database was 300°-600°C, however, several graphs contained data at temperatures slightly above or below this target—these data were included for completeness. The exposure time for each data point is included in the data. Although there are approximately 15,000 data points in the database, not all possible combinations of variables are included.

DATABASE DESIGN

After investigating the capabilities of several commercial database packages, it was decided that the corrosion database would be designed using Microsoft[®]

Access. As mentioned above, a review of the data presented in the collected articles revealed that the data could be broken down into three main categories: isothermal, cyclic temperature, and cyclic gases with or without temperature cycling. This fundamental division was incorporated into the design of the database. The basic structure of the database is based upon tables. The corrosion data collected was entered into three tables corresponding to the division discussed above.

The relationship among the tables is part of the database design and defines the types of questions the database can answer. A forms-based structure is provided to aid the end-user in asking the appropriate questions, called queries. This form structure guides the user through a series of steps in the query process. Each step asks the user to enter a value(s) or select an option(s). The user may go back to a previous form at any point in the process to make any appropriate changes. When all the forms have been completed a query is run on the chosen corrosion data table.

If no data in the database satisfies all the input parameters, a result that may be of interest to the user, a dialog box appears informing the user that no matches have been found. Alternate input values will need to be entered to locate any available data points. If the query does locates data, a results form appears on-screen listing the first value found. Navigation buttons are present on this form that allow the user to view all the records returned. The total number of records returned is also given. A revised query with smaller parameter ranges may be warranted if this value is too large. The user is given several options on how to proceed at this point.

First, the records found may satisfy the needs of the user without further modification. In this case the records may be printed. Second, the data records may be exported to a spreadsheet for further manipulation and/or to put the data into a graphical form. Third, as noted above, a modified query based on the results may be conducted. This third option can be repeated until the user is satisfied with the results. At this point the records may be printed out as in the first case or the data may be further manipulated as in the second case.

Another feature of the database is its capability to search the references by author and/or title keywords. Once the desired reference is located, the data extracted from the associated article are available for retrieval. These data are treated in the same way as the data returned by conventional queries as discussed above.

DATABASE CAPABILITIES

The capabilities of this database can best be illustrated through examples. The first example will also include several figures illustrating the forms used in building up a complete query. Please note that the references cited after the figure captions for the graphs are the sources of the data in the graphs.

Example 1 – Effect of changing temperature on corrosion rate in a constant gas mixture

This is a fairly simple database query that shows that the records in the database will yield results that are consistent with the known corrosion behavior of materials as the temperature increases. In this case a simple gas environment, H_2S , and two materials (carbon steel and 304 SS) with no smelt present are chosen as parameters for the query. The first form that appears when starting a query is shown as Figure 1.



Figure 1 Initial query form

Clicking on the Search button will bring up a second form that allows the user to select a query where all the parameters are required or one in which there is only one parameter needed. See Figure 2.



Figure 2 Second query form

In this case "Corrosion Data" is selected and then "OK" is clicked. This will open a third form, Figure 3, that allows the user to specify the environment.

On this form four options need to be chosen. For this example they are isothermal exposure, material by name, no smelt, and input gases. After these are selected, "OK" is clicked.

The form and associated subform buttons based on the selections on the Query selection form are shown in Figure 4. The two subforms associated with this form will pop up when the "Material" button and "Input Gases" button are clicked. The parameters required in the subforms must be entered before the "OK" button on the main form becomes active. The default values for temperature and time encompass the available range.



Figure 3 Third query form



Figure 4 Fourth query form

On the Materials subform, the option needed for this query example was to allow a particular material to be chosen from a category of materials. Selecting this option updates the subform to show the available categories. At this point a decision has to be made-select "all materials" because both carbon steel and a stainless steel are needed or run two separate queries.

Mate	rials Selection
-modola	
*	Select the option button corresponding to the
- Uardon sreeks	alloy category of interest. If all choices in a
Stainless steels	category are cranerest select the other butch.
C Low alloy steels	Salect Material by Composition on Duery
high aboy steels	Selection Options page
Nickel-base allows	
~ Model allays	
C Pure matale	 Select individual alloys from a category.
~ .	C Select on entire category
TAUFORAIQUAISIG SHOAR	
All materials	

Figure 5 Materials subform

"All materials" was selected and then "OK" clicked. A popup form then appears that allows the appropriate material selections to be made. The subform seen after updating and the pop-up form are shown in Figures 5 and 6.

Material	AI	C	Cr	Cu	Fe	Mn	Mc
C1018	0.05	0.18	0.05	0.02	98.85	0.77	0.04
304	0	0.08	19	0	68.6	2	0
SA-210	0	0.21	0	0	98.9	0.65	0
SA-192	0	0.12	0	0	99.1	0.45	0
304L	0	0.03	19	0	67.9	2	0
44							<u>+</u> [
61							
Litea City	single mai	HAT HOL	A CHCRI	nd fuu a	e uesire		
muttinia	plarhone f				rennar	CHE DOWN-	
	adiace	nt rance		narinza	4. 4.		

Figure 6 Materials pop-up

Clicking "OK" in the pop-up form returns the user to the main form. Clicking on the "Input Gases" button opens the associated subform shown in Figure 7.

nerum 182% 🗍	0	Homun CO28	Ũ	Minimum CD 🕱 🔰	0
antikum (9,2%; 🗍	100	Maximum CO2%	100	Maximum CO% 🗍	100:
launuur H25% 🦵	0	Minimum CH3SH%	0	Minimum \$8%	0
lsoiroumHXX2 [~	100	Маколко СНЗКНХ 🗍	100	Maximum 58%	100
tomenen 503%. 🗍	0	Hornun (CH3)25%	0	Minimum H2Q2 🗍	0
tантит 602% 🗍	100:	Maximuta (Crt3)25%	100	Maximum H20% 🗍	100
Manaan	H2% [O Mene	um CIZZ	0	
конка	1H2% (100 Маха	num (32%	100	
Min	nun HCPa	0 Masm	mHOS.	100	
Enter the ran	je in pi	arcent of the gase	a ptøse	nt in the enviro	ıment

Figure 7 Input Gases subform

This subform allows the user to set the range of gases present. Inert carrier gases are not included, therefore the total percentage does not have to add to 100%. After the desired gas ranges, in this case 100% H_2S , has been entered, clicking on "OK" returns the user to the main form.

The "OK" button is now active. Values are now entered for the temperature and exposure time. Clicking on the "OK" button runs the query based on all the parameter values that have been entered.

After a short time either a message telling the user that no matches were found in the data or a form showing the first record that contains data appears. If the message box appears, the user can modify the input parameters and rerun the query. If matching records are located, they appear in a form similar to that shown in Figure 8. The total number of records retrieved and navigation buttons are located at the bottom of the form.

For this example the data were exported to a spreadsheet for sorting and to present a summary of the data as a graph.

Meanum Cou	polon Rake 22 mpu Maamur Colosion Rate 2300	590
	ere are some rectors which may not have compared related	<u>a</u>
Hatenel	carbon steel	
Tempelakes	250 °C Pressule 1 dm Expessive Fine	15 hours
Inpul Gases	100% H25	
Calculated Eq	ulbolum Parcel Pressures: 6.889E-04 atm H2, 0 atm 02, 4.138E-07 atm 52	
Weight Gasic	ing/onf weight.css	юф'єр *
Çoxpoon Raje	130 mpy	
Rate Canalant		
Ciber		
î de	Kinetics of Reaction of Steel with Hydrogen Sulfide Hydrogen Mixtures	
eutras	Andrew Dravnieks and Carl H. Samans	
Jaumas Book	Journal of the Electrochemical Society	

Figure 8 Results form

As can be seen in Figure 9, the corrosion rates of both materials increase as the temperature increases, and the corrosion rate of carbon steel is greater than that of stainless steel. One could choose different materials to see their relative performance in this environment or one could do a query with a different gas environment with the same materials very easily.



Figure 9 Corrosion rate versus temperature for carbon steel and 304 stainless steel in 100% H₂S [5-7]

Example 2 – Effect of changing S_2 pressure at constant temperature

This is a slightly more complicated database query. While it is no harder to fill out the query forms than in the previous example, a little more thought is required to decide how to limit the number of records retrieved. Once a search strategy has been adopted, everything proceeds as described in the previous section. Figure 10 shows the results for carbon steel at different temperatures. The main result that may be drawn from this plot is that while the corrosion rate of carbon steel is affected by the S₂ partial pressure, large changes are required. However, it is very clear from the figure that a change in temperature has much greater influence on the corrosion rate than does a change in S₂ partial pressure. Figure 11 shows the results of the same query in a narrower S₂ partial pressure range where this effect is emphasized.

Figure 11 shows the results of the same query in a narrower S_2 partial pressure range where this effect is emphasized.



Figure 10 Weight gain versus log of S₂ partial pressure for carbon steel at various temperatures [4, 8]



Figure 11 Weight gain versus log of S₂ partial pressure for carbon steel at various temperatures [4, 8]

CONCLUSIONS

A forms-based, user-friendly corrosion database for use by recovery boiler operators has been developed. This database contains information extracted from the published literature on the corrosion of many materials in environments of interest for recovery boiler operation. The database can be used as an aid in material selection for a particular environment or may be used to predict the behavior of a material in a variety of environments. The results of any query can be viewed on-screen and may be printed. The results of the queries can be exported to other databases or plotted in a graphical form defined by the user.

ACKNOWLEDGEMENTS

The Department of Energy (through grant DE-FC36-95GO10092) and the American Forest and Paper Association (AF&PA) have provided financial assistance for this project. Technical advice and guidance was received from members of the AF&PA Recovery Boiler Technical Advisory Group on Corrosion and Mr. Doug Singbeil of PPRIC. Special thanks to Dr. Jeffery Colwell of Battelle for his constructive criticism of the database design during development.

REFERENCES

1. Singbeil, D., Frederick, L., Stead, N., Colwell, J., and Fonder, G., "Testing the Effects of Operating Conditions on Corrosion of Water Wall Materials in Kraft Recovery Boilers," 1996 TAPPI Engineering Conference Proceedings, Vol. 2, TAPPI PRESS, Atlanta, p. 649

2. Plumley, A.L, Lewis, E.C., and Tallent, R.G., *TAPPI Journal*, "External Corrosion of Water-Wall-Tubes in Kraft Recovery Furnaces," **49**(1): 72A (1966)

3. "Investigation of Alloyed Steels for Use in Black Liquor Recovery Boilers," Joint report from the Swedish Corrosion Institute, project 269060, and the Finnish Recovery Boiler Committee, Reports 1-4, 1971-2

4. Stelling, O., and Vegeby, A., *Pulp and Paper Magazine of Canada*, "Corrosion on Tubes in Black Liquor Recovery Boilers," **70**: T236 (Aug. 1, 1969)

5. Sorell, G., and Hoyt, W.B., *Corrosion*, "Collection and Correlation of High Temperature Hydrogen Sulfide Corrosion Data," **12**: 213t (1956)

6. Dravnieks, A., and Samans, C.H., *Journal of the Electrochemical Society*, "Kinetics of Reaction of Steel with Hydrogen Sulfide-Hydrogen Mixtures," **105**: 183 (1958)

7. Kremer, G., and Volk, K.E., *Stahl und Eisen*, "Die Hestellung und Verwendung von hitzebeständigen Aluminiumüberzügen," **66-7**: 250 (1947)

8. Backensto, E.B., Drew, R.E., Prior, J.E., and Sjoberg, J.W., *Corrosion*, "High-Temperature Hydrogen Sulfide Corrosion on Stainless Steels," **14**: 27t (1958)