CONTROL OF KILN CORROSION AT WOOD PRODUCTS PLANTS

Regis R. Rumpf
Product Manager
Boiler Water Treatment
DREW INDUSTRIAL DIVISION
ASHLAND CHEMICAL, INC.

INTRODUCTION

Wood Products Plants such as plywood and sawmill operations commonly use dryers and kilns to remove moisture from wood. Some of these units are direct fire heated; however, steam heated units are the most prevalent in use today. Corrosion in these steam heated dryers and kilns can sometimes be severe. The severity of the corrosion and subsequent potential failure is directly proportional to the quantity of dissolved oxygen and/or carbon dioxide carried by the steam. Operational adjustments as well as the use of multi-functional, non-toxic corrosion inhibitors were utilized for corrosion control in this study. The use of this MEKO (methyl ethyl ketoxime) based inhibitor system (See Figure 1) yielded a significant decrease in condensate corrosion rates and eliminated the associated health risks from the prior hydrazine-containing product. (See Figure 2)

BASIC PROCESS

After logs are delivered to the plant, they are stacked, and depending upon holding time, they are kept moist by spraying a fine mist of water on them to prevent splitting.

The first stage in processing is debarking. This is usually accomplished by passing logs through a rotating drum. In this process, the bark is stripped and sent to the fuel house while the logs are sent to the saw mill operations. It is important to note that sub-processes may be used to separate sand and grit before sending the bark to the fuel house. If sand and dirt are allowed to pass with the bark, deposition problems may occur in the fireside of boilers. Severe fireside deposition may cause fireside flow restrictions resulting in "hot spots" in the boiler as well as reduced steaming capacity. To help alleviate deposition problems, some plants utilize soot blowers. In addition, they may also incorporate fuel additives such as slag modifiers to minimize deposition.

The next step after debarking is the culling and sawing of logs. Today's modern plants incorporate computers to automatically cull, size, and cut logs. Scraps sometimes referred to as "lillypads" are sent to a chipper to be used by paper mills for pulp or particle board. These scraps are also used at oriented strand board plants as a raw material or as a fuel for the boiler house.

Logs suitable for plywood are then immersed in vats to soften them for easier turning in the lathe. Vats contain water along with alkaline chemicals to improve the softening of the wood. Water is heated either through direct steam injection or through heat exchangers that improve boiler efficiency and reduce plant water outfall by returning steam as condensate. Heat exchangers, however, can develop leaks allowing vat water to enter the boiler water system resulting in deposit problems. Weekend shutdowns also allow for corrosion to occur, causing elevated iron levels in the condensate returned to the boilers during start-up. Since most of the equipment in these plants operates cyclically, this on-off operation makes the steam and condensate system prone to oxygen corrosion when atmospheric oxygen is pulled into the system during off periods.

In modern plywood plants, logs are then automatically picked up and turned on the lathe. This process is monitored by operators but performed by computers which automatically adjust log position for the most efficient cut. The veneer sheets are separated from the strips and cut to length. Strips are typically hand-pulled and sent through a string machine to tie the strips together in one sheet to form the plywood core. Log cores from the lathe are either sent to the chipper or cut into landscape timbers, poles, or studs.

Veneer and strips are then sent to individual dryers that may be either steam or gas fired. Wood passes on a continuous conveyor through the dryers and the speed is adjusted automatically to insure proper wood dryness at the dryer exit. This process is one of the most critical areas in the plant. Steam dryers are most prevalent due to their lower operating costs. Bottlenecks may occur in this area of the plant if dryer performance is degraded. Steam traps must be properly sized to prevent "water logging" and boiler water levels, boiler water chemistry, and steam separating equipment must be kept within design to prevent carryover of boiler water to the dryers.

After glue is applied, veneer and strips are then brought together to make plywood that enters the pre-press to help insure bonding of the veneer and strand layers. After the pre-press operation, plywood then enters the hot press. Here, hydraulic pressure is applied with hot platens that are normally steam heated. The combination of pressure and temperature completes the plywood bonding process. As in the dryer, both steam trap sizing and boiler water carryover are important to the efficient operation of the press. Corrosion in the condensate, while generally less of a factor, must also be considered for equipment reliability.

To complete the process, plywood is cut to dimension, graded, and in specialty mills, may be grooved and/or sanded. The scraps and sawdust are then sent to the boiler as fuel. Sawdust burning must carefully be controlled to prevent explosion in storage. The high heat given off in burning sawdust must be considered to prevent overheating problems in the boiler. Glue present in plywood trim and sand in sawdust both may contribute to fireside deposition problems.

Cores from the lathe are chipped, or cut into landscape timbers or studs. Both the landscape timbers and studs are usually dried in a kiln. The batch process employed both in sawmill and plywood mills in operating steam driven kilns creates corrosion problems by allowing oxygen to enter between batches or during the cool-down periods. "Water logging" must again be controlled through the proper sizing of the steam traps and prevention of boiler water carryover.

Corrosion must be kept under control in the condensate system to minimize iron and copper levels. Otherwise, metal oxides transported into the boiler increase the potential for deposition and subsequent boiler failures. Figure 3 provides a schematic of the mill operations.

DISCUSSION

The combination of oxygen and/or carbon dioxide is the direct cause of dryer and kiln corrosion.

Oxygen corrosion is most commonly caused by the ingress of oxygen during the cooling-off periods between loading kilns and/or the periodic shutdown of equipment. Oxygen enters the condensate system during off periods because of the vacuum formed as steam condenses while the system is cooling-off. Typical indication of oxygen corrosion is the deep pitting of metal surfaces.

Carbon dioxide corrosion is caused by the formation of carbon dioxide in the boiler through the breakdown of carbonate and bicarbonate alkalinity. Carbon dioxide volatilizes with the steam to ultimately condense in the dryers or kiln condensate to form carbonic acid. The amount of carbon dioxide formed is directly related to the type and amount of alkalinity present in the boiler water makeup. The concentration distribution of carbon dioxide in the steam and condensate system will vary throughout the plant. Carbon dioxide will condense more readily in areas of the plant where a reduction of pressure occurs or where lines dead-end. In dryers, the distribution of carbon dioxide can typically be seen by measuring condensate pH at several different sections of the dryer or in kilns by measuring pH at the different kilns in operation. An indication of carbon dioxide caused corrosion is thinning of metal surfaces known as "grooving" at and below the water line in the condensate system. Steam lines are not affected by carbon dioxide because carbon dioxide must first condense with water to form carbonic acid.

It is important to note that the combination of oxygen and carbon dioxide corrosion is negatively synergistic, i.e., the net effect of combinations of these "bad actors" is 6-10 times the corrosion rate when each is taken individually. In addition, the release of carbon dioxide makes this corrosion reaction self-perpetuating. Figure 4 summarizes these corrosion reactions.

SYSTEM

The makeup water for this South Central Wood Products Plant is sodium zeolite softened and dealkalized through a strong acid cation exchange unit operated in the hydrogen form. The effluent is degasified to reduce the makeup total alkalinity to under 50 ppm. This makeup and 50% condensate return are then deaerated. The resulting feedwater contains approximately 25 ppm of total alkalinity.

One powerhouse consisting of 4 keeler "D" type watertube boilers supplies 300 psig steam to the dryers and 150 psig steam to the kilns. Each boiler has a rated capacity of 110,000 lbs./hr. with an average total steam output of 280,000 lbs./hr. Figure 5 summarizes the boiler water system.

MECHANICAL IMPROVEMENTS

Maintaining proper operation of the entire boiler water system including the deaerator will minimize chemical treatment requirements. Other mechanical processes such as dealkalization, dumping condensate following start-up, keeping steam flow on during plant down periods, and controlling water logging by proper sizing of steam traps as well as the prevention of boiler water carryover all contribute significantly to the minimization of system corrosion.

CHEMICAL TREATMENT CONSIDERATIONS

This mill's previous internal chemical treatment program consisted of a combination of polyphosphate supplemented with a sludge conditioner. In addition, catalyzed hydrazine was fed as the primary feedwater oxygen scavenger and neutralizing amines were fed to the afterboiler system to elevate condensate pH. Corrosion rates were monitored on an ongoing basis utilizing mild steel corrosion coupons. Results averaged 8.2 mpy and 5.0 mpy for the kilns and dryers, respectively. Total iron levels in the composite returned condensate were consistently greater than 0.10 ppm as Fe. In addition, the presence of oxidized iron in the dryer and kiln condensate samples was established utilizing membrane filter studies.

CURRENT PROGRAM

Less than satisfactory performance results as well as OSHA's initiation of the Hazard Communication Standard increased the plant's awareness regarding the use of hydrazine. The chemical treatment program was subsequently switched to a MEKO based corrosion inhibitor product. This highly effective combination treatment utilizes a synergistic blend of filming amine, neutralizing amines and MEKO volatile oxygen scavenger/metal passivator to minimize both low pH and oxygen corrosion in the steam condensate system.

The filming amine forms a monomolecular barrier between metal surfaces and the potentially corrosive condensate. The neutralizing amines elevate the condensate pH and aid in the distribution of the filmer.

MEKO scavenges oxygen throughout the condensate system and provides additional protection to the preboiler system via condensate return. In addition, MEKO passivates the metal surfaces of the entire boiler water system imparting corrosion resistance. This blend of MEKO, filming amine and neutralizing amines was fed directly to the steam header and was significantly more effective in protecting the condensate system than the previous program. Condensate corrosion rates, as determined by corrosion coupons, were reduced to average values of 0.3 mpy and 0.1 mpy for the kilns and dryers, respectively. Condensate iron values have consistently been in the 5-20 ppb range since the program change. In addition, there was no evidence of oxidized iron in the returned condensate from the dryer and kiln areas after switching to the MEKO-based product (See Table 1). This is attributed to MEKO'S greater volatility and higher distribution ratio (See Tables 2 and 2A) with respect to hydrazine as well as comparable passivation and superior oxygen scavenging (See Figures 6, 6A and 7). Furthermore, there was an overall 25% cost reduction associated with the new program.

SUMMARY

Methyl ethyl ketoxime-based condensate treatment effectively controls oxygen and carbonic acid induced corrosion in wood processing kilns and dryers. This chemistry demonstrates superior performance as compared to the previous hydrazine-based program as illustrated by lower corrosion rates and condensate iron and copper values.

Added benefits of this new program include the elimination of safety hazards and the associated health risks from the use of hydrazine, reduction of condensate corrosion rates and reduced chemical treatment costs.

BIBLIOGRAPHY

1. Weiss, C.O. and Emerich, D.E. "Oximes as Oxygen Scavengers", U.S. Patent #4,487,745.
2. Principles of Industrial Water Treatment, Drew Chemical Corporation, Boonton, New Jersey, 1988.
3. Cappabianca, C.J., Pelosi, P.F., and Nulty, J.H., "Experience With a Novel, Volatile Boiler Water Oxygen Scavenger", International Water Conference, Pittsburgh, PA, Nov. 4-7, 1985.
4. Pelosi, P.F. and Beecher, J.S., "The Chemistry of Hydrazine and Methyl Ethyl Ketoxime Under Hydrothermal Conditions", Corrosion '86, Houston, TX, March 17-21, 1986.
5. Cappabianca, C.J. and Beecher, J.S., "Update on the Chemistry and Applications of Methyl Ethyl Ketoxime, "Corrosion '87, San Francisco, CA, March 9-13, 1987.
6. Noack, M.G., "Oxygen Scavengers", Corrosion '89, New Orleans, LA, April 17-21, 1989.
7. Rondum, K.D., Fuller, E.J., and DeWitt-Dick, D.B., "Field Operating Experiences with a Unique Volatile Oxygen Scavenger/Metal Passivator in a High Pressure Utility Circuit", International Water Conference, Pittsburgh, PA, Oct 23-25, 1989.
8. Gonzalez, W.J., Monette, J.C., and Rondum, K.D., "Field Experiences Relative to Corrosion Monitoring In Evaluating Oxygen Scavenger Efficacy ", Corrosion 90, Las Vegas, Nevada, April 23-27, 1990.

Table 1

Corrosion Data

Observations	Before MEKO	After MEKO
Avg. Kiln CR *	8.2 mpy	0.3 mpy
Avg. Dryer CR *	5.0 mpy	0.1 mpy
Avg. Condensate Fe **	80-120 ppb	5-20 ppb
Avg. Condensate Cu **	10-20 ppb	0-5 ppb
Oxidized Iron ***	Present	None Detected

* Weight loss (12 coupons averaged)
** Atomic absorption (120 samples averaged)
*** Millipore filter methodology

Table 2

Distribution Ratios of Various Corrosion Inhibitors

Chemical	Distribution Ratio *	pH of Test Solution
MEKO	8.3 +/- 0.5	7.5
	7.6 +/- 0.2	10.0
	9.8 +/- 0.8	12.0
Hydrazine	0.0036 +/- 0.0006	7.5
	0.019 +/- 0.003	10.0
	0.023 +/- 0.003	12.0
Morpholine	0.47	12.0
Diethyl Aminoethanol	4.28	12.0
Cyclohexylamine	28.5	12.0

* Atmospheric Pressure, 212 deg F, Equivalent Chemical Concentrations in Boiler Water

Table 2A

Distribution Ratios of Various Corrosion Inhibitors

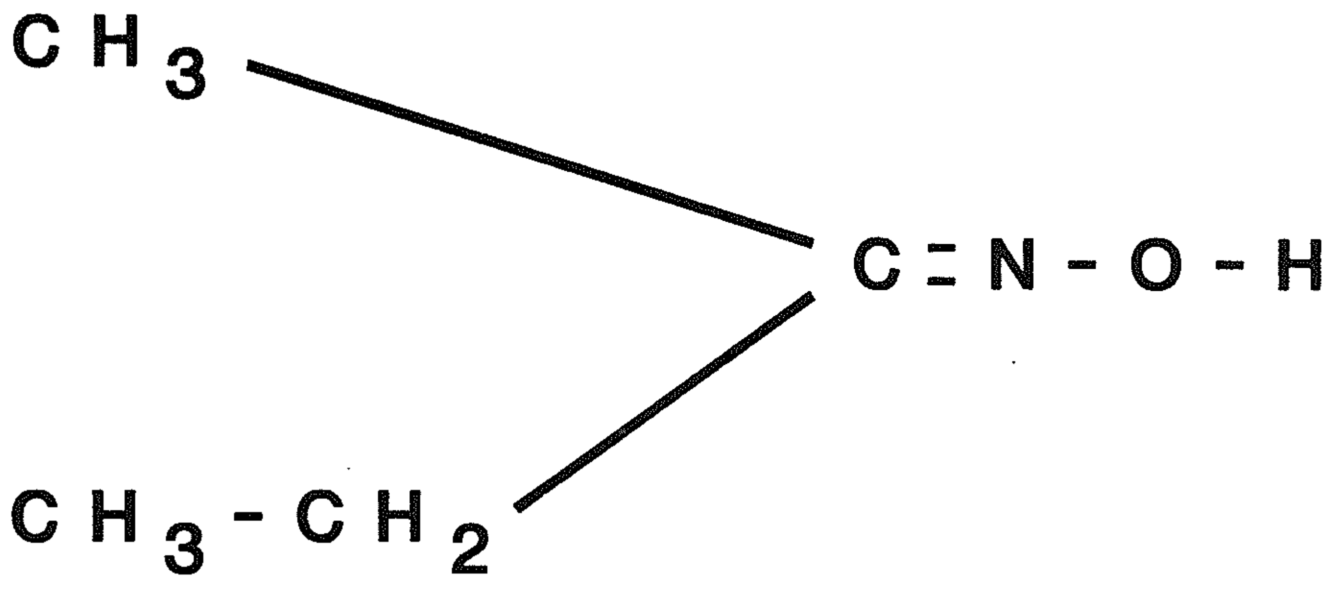
Chemical	Distribution Ratio *	"Industry Standard"
Sulfite	0	0
Erythorbate	0	0
Hydroquinone	0	0
Carbohydrazide	0	0
Hydrazine	0.02	0.1
Morpholine	0.5	0.4
Diethyl Hydroxylamine	5.4 **	1.3
DEAE	4.3	1.7
MEKO	9.8	2.2
Cyclohexylamine	28.5	4.0

* Atmospheric Pressure, 212 deg F, Boiler Water pH = 12.0
Equivalent Chemical Concentrations in Boiler Water

** Estimate

Figure 1

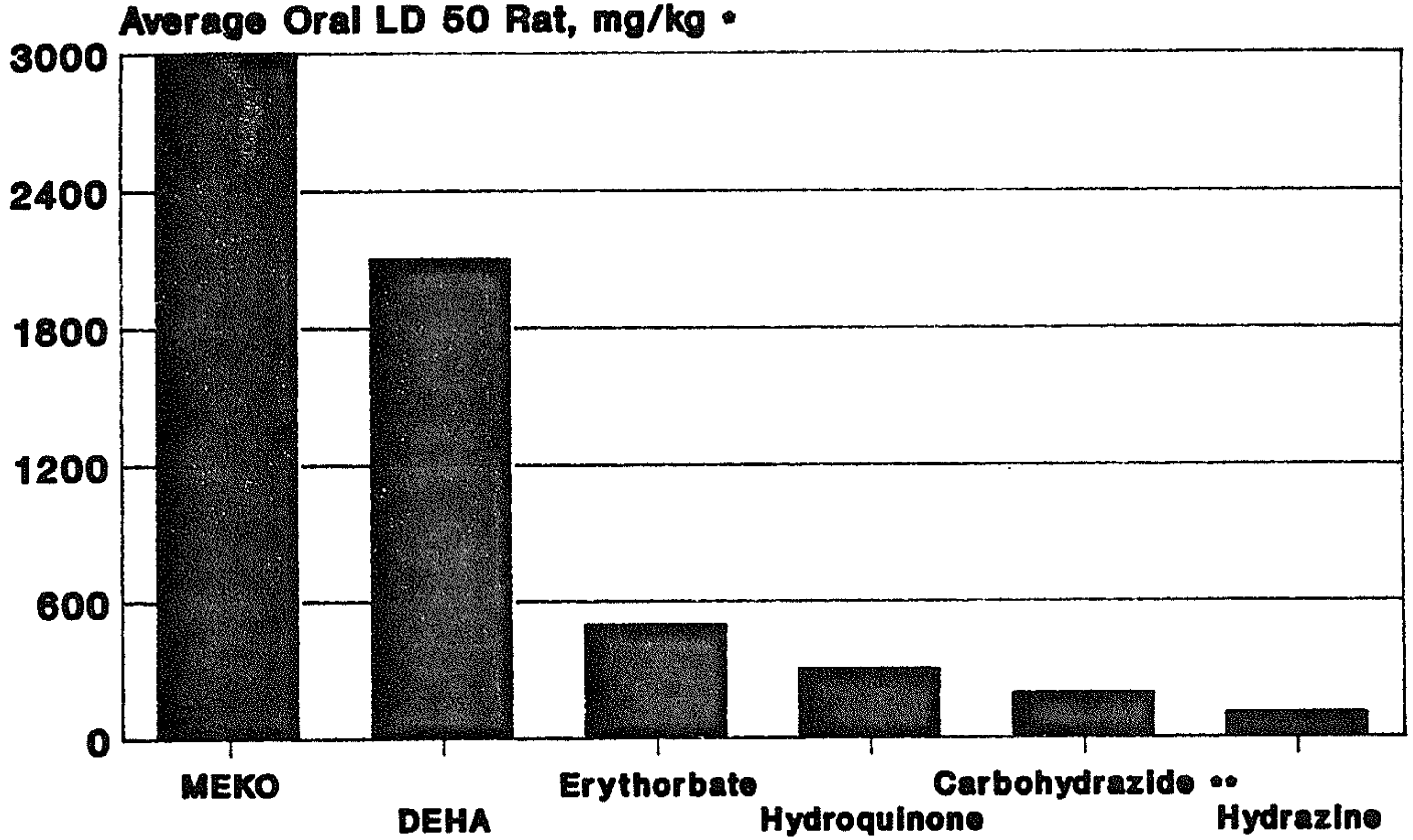
The Structure of Methyl Ethyl Ketoxime



Methyl ethyl ketoxime
(MEKO)

Figure 2

Relative Oxygen Scavenger Safety



* Interperitoneal LD Lo Mouse, mg/kg

** Carbohydrazide begins releasing hydrazine at ambient temperatures.

Figure 3
Flow Diagram of Plywood Mill Operations

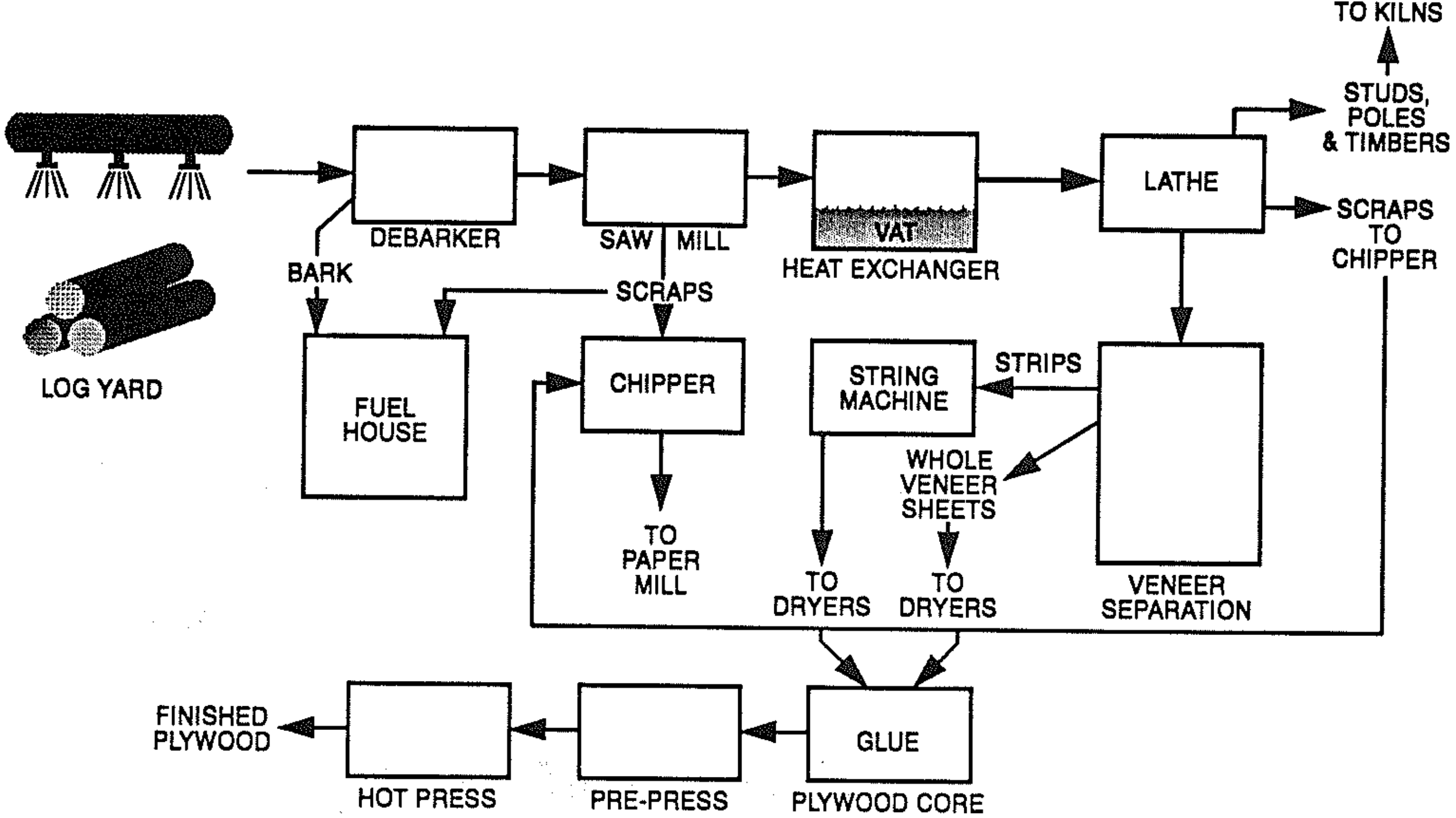


Figure 4

Corrosion Reactions

Oxygen Corrosion:

$$4\ Fe_3O_4 + O_2 \longrightarrow 6\ Fe_2O_3$$

Low pH Corrosion:

Alkalinity Breakdown

$$2\ HCO_3 + Heat \longrightarrow CO_3 + H_2O + CO_2$$

$$CO_3 + H_2O + Heat \longrightarrow 2\ OH + CO_2$$

Carbonic Acid Formation & Corrosion

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$2\ H_2CO_3 + Fe \longrightarrow Fe(HCO_3)_2 + H_2$$

$$4\ Fe(HCO_3)_2 + O_2 \rightarrow 2\ Fe_2O_3 + 8\ CO_2 + 4\ H_2O$$

Figure 5
Flow Diagram of Boiler Water System

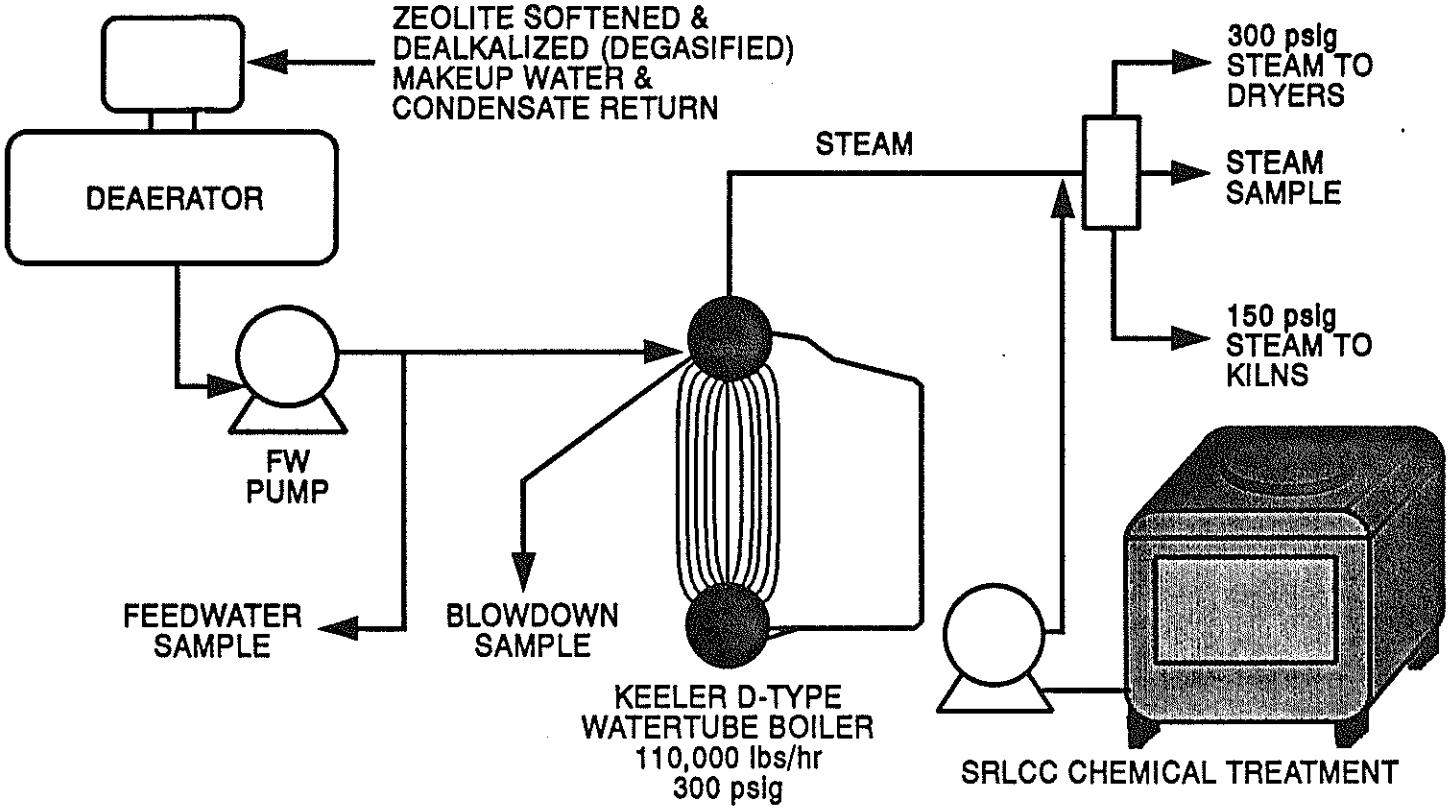


Figure 6

MEKO Reactions

As an Oxygen Scavenger:

$$2\ \text{MEKO} + O_2 \longrightarrow \text{Methylethylketone (MEK)} + N_2O + H_2O$$

As a Metal Surface Passivator:

$$2\ \text{MEKO} + 6\ Fe_2O_3 \longrightarrow 4\ Fe_3O_4 + 2\ \text{MEK} + N_2O + H_2O$$

$$2\ \text{MEKO} + 4\ CuO \longrightarrow 2\ Cu_2O + 2\ \text{MEK} + N_2O + H_2O$$

Figure 6A

Hydrazine Reactions

As an Oxygen Scavenger:

$$N_2H_4 + O_2 \longrightarrow 2\ H_2O + N_2$$

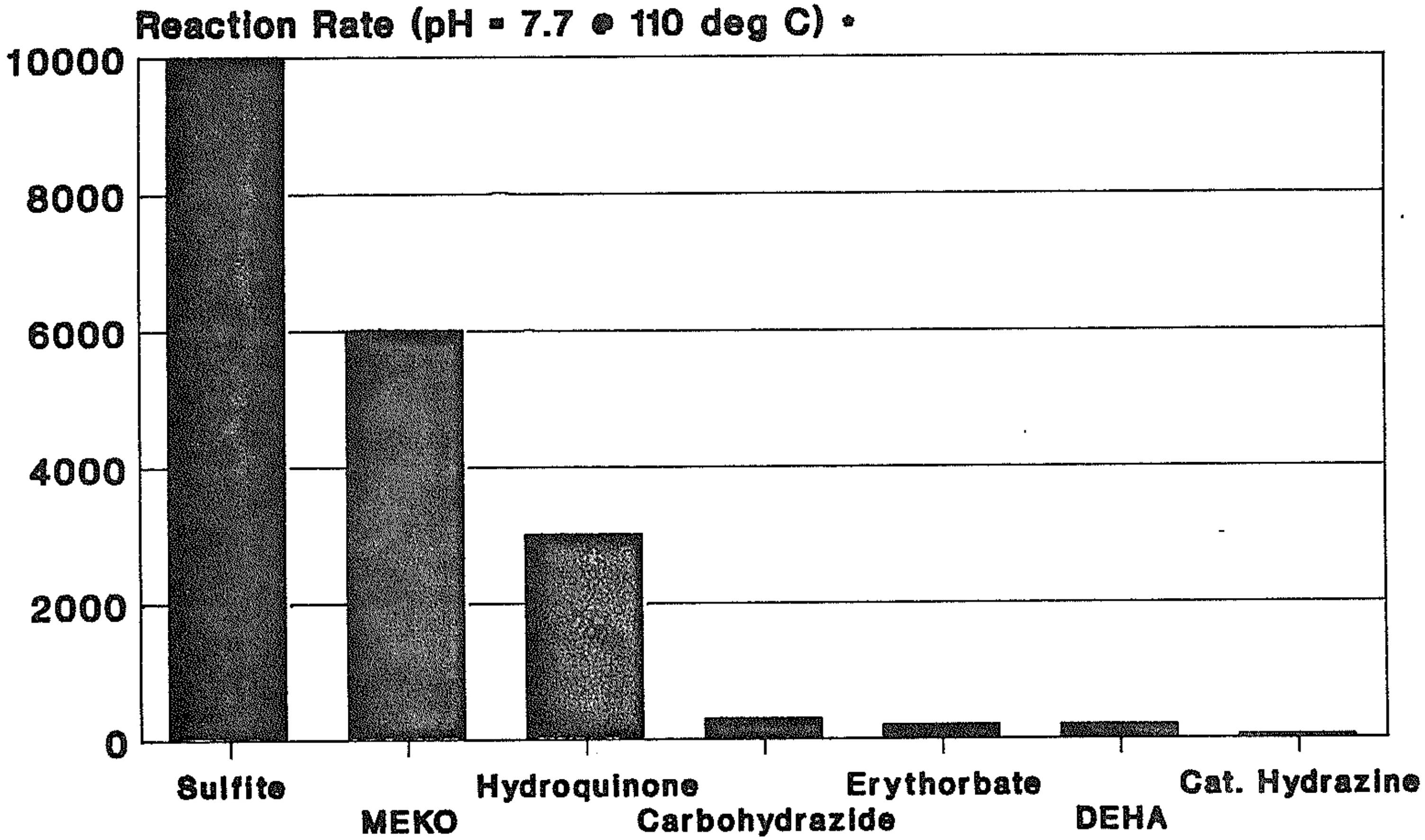
As a Metal Surface Passivator:

$$N_2H_4 + 6\ Fe_2O_3 \longrightarrow 4\ Fe_3O_4 + 2\ H_2O + N_2$$

$$N_2H_4 + 4\ CuO \longrightarrow 2\ Cu_2O + 2\ H_2O + N_2$$

Figure 7

Relative Oxygen Scavenging Efficacies



* Overall rate constant, speed of reaction with dissolved oxygen, extrapolated with Arrhenius equation to 110 deg C. Units are reciprocal moles (M) and minutes (min), thus second order reaction overall.