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Bayer Process Heat Exchangers Cleaning
Efficiency: Optimizing the Acid
Dissolution of Sodalite Scale

Sébastien Fortin
Alcan International Limited

Raymond Breault
Alcan International Limited

BAYER PROCESS HEAT EXCHANGERS CLEANING EFFICIENCY: OPTIMIZING THE ACID DISSOLUTION OF SODALITE SCALE.

Sébastien Fortin and Raymond Breault

Arvida Research and Development Center, Alcan International Limited,
1955 boul. Mellon, Jonquière (Québec), Canada, G7S 4K8
e-mail: sebastien.fortin@alcan.com, raymond.breault@alcan.com

ABSTRACT

Aluminum metal is produced by the electrolytic reduction of aluminum oxide (Al_2O_3), mainly extracted from bauxite ore digested in a hot caustic soda solution. This solution is supersaturated with respect to sodium aluminate and silicate, which react together to form sodalite ($3[\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}]\cdot\text{Na}_2\text{CO}_3$) at high temperatures. Heat exchanger tubes are scaled with this compound, which seriously reduces heat transfer coefficient, thus increasing energy costs.

Heat exchanger tubes are cleaned periodically with a sulfuric acid solution that contains a corrosion inhibitor. An investigation was undertaken in order to study the parameters affecting sodalite scale dissolution by sulfuric acid: temperature, solution concentration, flow rate, etc. A custom-made set-up was used, simulating a heater cleaning operation, using scaled tube sections as test specimens.

It was found that by increasing the temperature, the flow rate and the acid concentration, the scale dissolution rate increases. However, it was also determined that the presence of a corrosion inhibitor reduces the efficiency of the cleaning operation at high temperatures. This result was further investigated by adding organic compounds to the sulfuric acid solution.

INTRODUCTION

The Bayer Process

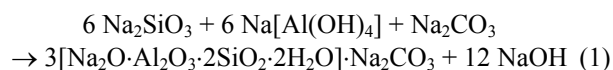
The Bayer process was patented more than 100 years ago by Karl Josef Bayer (Bayer, 1888) and it has been used since to obtain aluminum oxide from bauxite. In low temperature plants, bauxite ore is digested in concentrated caustic soda (NaOH) solutions at 140-150°C, in pressurized vessels. This step is in fact the dissolution of gibbsite (alumina trihydrate, commonly named “hydrate”, $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$; chemically: $\text{Al}(\text{OH})_3$), as sodium aluminate ($\text{Na}^+[\text{Al}(\text{OH})_4]^-$). After appropriate decantation and filtration steps to separate the insoluble materials, the supersaturated solution (pregnant liquor) is cooled down to 65°C and seeded with gibbsite crystals in order to accelerate the precipitation of hydrate. The product is then separated and calcined to obtain pure alumina (Al_2O_3), mainly used in smelters for the production of aluminum. After precipitation

of hydrate, the Bayer liquor is returned to digestion through a multiple-step heat-exchange circuit (Authier-Martin et al., 2001; Pearson, 1955).

Since the caustic solution is continuously supersaturated with respect to sodium aluminate and silicate, scale is present in every part of the process. Thus, scale has always been an important matter of concern in Bayer plants, especially in heat exchangers because of its deleterious effects on energy consumption (Delgado et al., 1992). Since the solution is alternately heated up and cooled down in the Bayer circuit, heat exchange is extremely important in terms of energy costs.

Scaling of the Heat Exchangers

As the temperature of the solution increases in the heat exchangers, sodium aluminate and silicate react to form sodalite scale (Jamialahmadi et al., 1993) on vessel walls (heater tubes and other pipes), according to the chemical reaction expressed by Equation 1 (Duncan, Müller-Steinhagen et al., 1995; Zheng et al., 1997). Notice that CO_3^{2-} in sodalite is sometimes substituted by other anions (Cl^- , SO_4^{2-} , etc.).



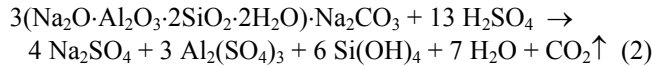
Chemically, Bayer sodalite is a sodium aluminosilicate, consisting of $([\text{AlSiO}_4]^-)_n$ cages of the zeolite type. It is currently named the “desilication product” (DSP), since it eliminates dissolved silica from Bayer liquor. Moreover, the driving force to the formation of sodalite is the silica supersaturation (Duncan, Groemping et al., 1995).

Sodalite scale is a very poor thermal conductor: 0.3 W/m·K (Müller-Steinhagen et al., 1994). It was previously reported that a thin layer of 1 mm of sodalite scale reduces heat transfer coefficient by 77% (Delgado et al., 1992). Its impact on heat transfer is thus quite important. It is estimated that about 80% of the costs related to heat exchangers scaling are due to the additional energy required to re-heat liquor to the required digestion temperature.

Typically, heat exchangers that are scaled with Bayer sodalite are regularly cleaned with diluted sulfuric acid solutions (Jamialahmadi and Müller-Steinhagen, 1992; Yamada et al., 1985) to recover their initial heat transfer coefficient and avoid tube blockages. A corrosion inhibitor

is generally added to the cleaning solution to minimize corrosion of the carbon steel tubes and the other parts in contact with the acid solution.

The dissolution of sodalite scale by sulfuric acid is relatively straightforward and can be expressed by the following chemical reaction:



A systematic study of the parameters that influence the sodalite scale dissolution was undertaken in order to optimize the method used to clean the heat exchangers. The parameters that were studied are: concentration of acid, temperature, flow rate, additives to the sulfuric acid solution, amount and nature of the corrosion inhibitor. The results of this study are presented herein.

EXPERIMENTAL METHODS

Experimental Set-up

Laboratory experiments were conducted using a custom-made set-up that simulates the cleaning of one heat exchanger tube. The solution is kept at a constant temperature in a water bath that contains a 3-liter capacity acid tank. The solution is circulated through the test specimen using a peristaltic pump with an adjustable flow rate. The test specimen is a 4-inch long section of a blocked heat exchanger tube from Alcan Vaudreuil Works. Each specimen has been drilled along the axis with a 1/2", 3/4" or 1" diameter bit so that the amount of scale is known. The following scheme illustrates the set-up.

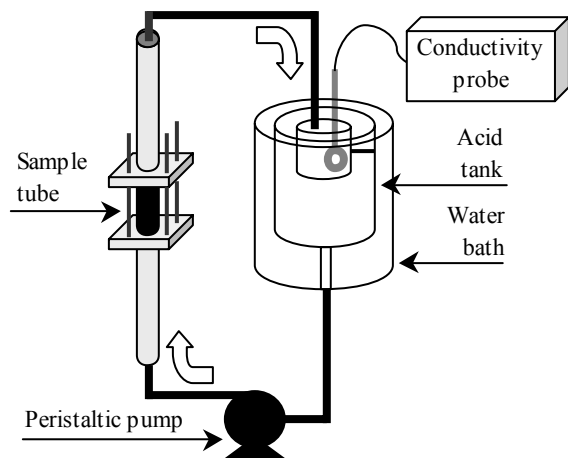


Fig. 1 Schematic illustration of the experimental set-up.

Analyses and Methods

The acid concentration is monitored by an electrodeless *Foxboro* conductivity probe ("donut" type), model 871-EC with a *Foxboro* analyzer, model 875-EC. The conductivity probe was calibrated by titration of the sulfuric acid solution with sodium hydroxide in the presence of excess potassium fluoride (phenolphthalein is used as a turning point indicator). When required by experimental designs, the concentration of dissolved aluminum, silicon and sodium has been determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). A *Cambridge* instrument equipped with a *Pentafet* detector was used for scanning electron microscopy analyses.

The dissolution rate is expressed as grams of scale dissolved per minute, based on the first part of the experiment, during which the acid consumption is rather linear. This is represented by the thick section of the following graph.

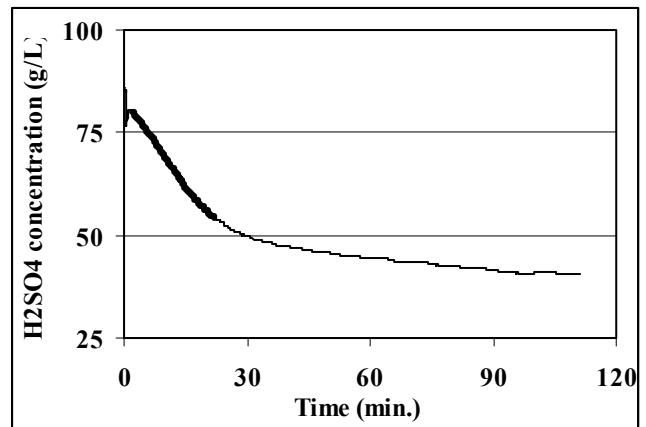


Fig. 2 Sulfuric acid concentration as a function of time. The dissolution rate is based on the thick line.

The cleaning efficiency is measured by the proportion of scale that is dissolved ($M_{\text{start}} - M_{\text{end}}$), expressed as a percentage of the total amount of scale present in the tube:

$$\text{dissolution}(\%) = \frac{M_{\text{start}} - M_{\text{end}}}{M_{\text{scale}}} \times 100 \quad (3)$$

RESULTS

Effect of the Flow Rate on Scale Dissolution

As expected, increasing the acid solution flow rate accelerates the sodalite scale dissolution (see Fig. 3).

The results show that, at the laboratory scale, for each increase of the volumetric flowrate of 1 L/minute, an additional 0.4 g of scale is dissolved every minute. This means that a 100% increase of the flow rate would cause approximately a 20% increase of the dissolution rate.

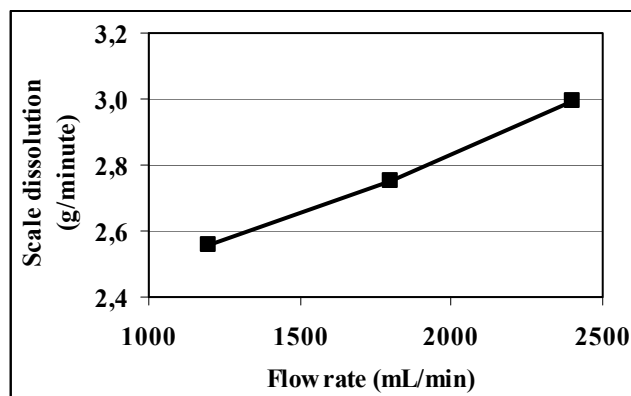


Fig. 3 Scale dissolution rate with increasing acid solution flow rate.

Such a small gain is not very useful for heater cleaning, because acid circulation is a small fraction of the total heater downtime. However, for the cleaning of heavily scaled lines which often contain several tons of sodalite scale, there is surely a gain in increasing the flow rate in order to dissolve more scale in a short time. These cleaning operations are done during maintenance plant shut-downs, when time is of primary importance to minimize production losses.

Acid Concentration

Equation 2 shows that 13 moles of H_2SO_4 dissolve 1 mole of sodalite. It is then expected that increasing the acid concentration is an easy way to accelerate the dissolution rate of sodalite scale. The results shown in Fig. 4 are thus not surprising.

In the laboratory experiments, we have observed that a 25% increase of the acid concentration (from 120 to 150 g/L) accelerates the scale dissolution rate by 25% as well.

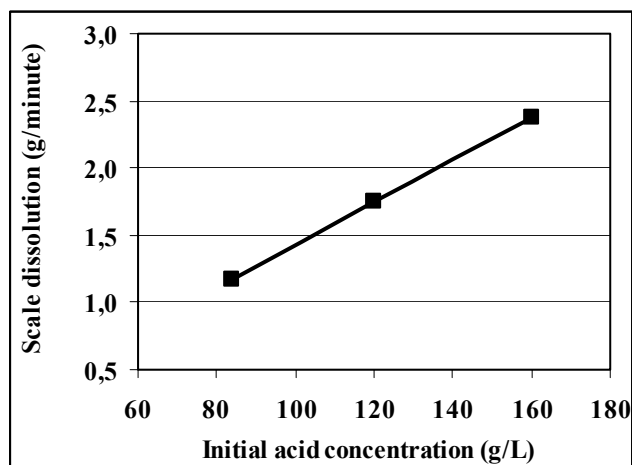


Fig. 4 Scale dissolution rate with increasing initial acid concentration.

This way of accelerating scale dissolution should however be used with caution, since corrosion of the mild steel tubes will also be favored by the higher acid concentration, despite the presence of a corrosion inhibitor (which is usually not 100% efficient).

Moreover, preparing a more concentrated acid batch in the plant will increase the solution temperature because of the exothermic dissolution process of sulfuric acid in water. The next section gives more details about the importance of controlling the solution temperature.

Temperature of the Solution

According to the Arrhenius equation ($k = Ae^{-E^*/RT}$), chemical reaction rates are increased at higher temperatures. Sodalite scale dissolution is no exception, as shown in Fig. 5. For example, increasing the solution temperature from 35 to 45°C increases the dissolution rate by about 35%.

This could be an appreciable gain, even more so if it is combined with a higher acid concentration and/or a higher flow rate, as specified in the previous sections. However, one should keep in mind that corrosion is also favored by higher temperatures and that acid circulation time is not a major issue for heat exchanger cleaning. Increasing the temperature could, however, be considered for line descaling operations.

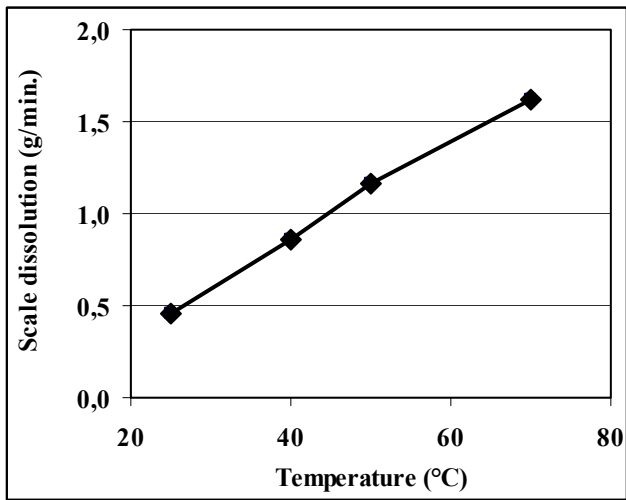


Fig. 5 Scale dissolution rate with increasing temperature.

Corrosion Inhibitor

The corrosion of mild steel by sulfuric acid is well documented and the use of a corrosion inhibitor is a widespread practice. A broad spectrum of pretty efficient corrosion inhibitors are available for various applications (Roberge, 2000; Sastri, 1998). Our experiments nevertheless revealed an unexpected effect of the corrosion inhibitor in the course of sodalite scale dissolution.

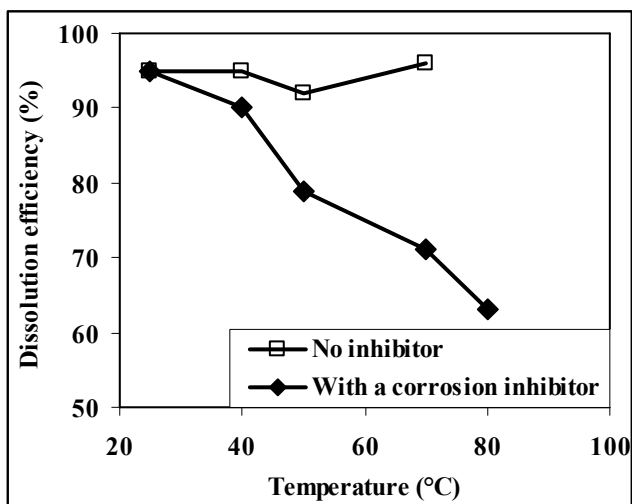


Fig. 6 Percentage of dissolved scale with increasing temperature, with and without corrosion inhibitor.

As seen in the previous section, a higher temperature systematically increases the dissolution rate of sodalite scale. A high dissolution rate, however, is not the only parameter to consider. In fact, because a much better heat transfer coefficient is obtained when a heat exchanger is not scaled at all, a total scale removal is of primary importance in terms of energy savings. As shown in Fig. 6, it was observed that the presence of a corrosion inhibitor becomes a significant obstacle to cleaning efficiency as the temperature increases.

These results clearly demonstrate that the sodalite scale dissolution is incomplete when the corrosion inhibitor is present and that it depends on the temperature. This phenomenon is of utmost importance, since more scale is left undissolved on the tube wall when the solution temperature is too high. Remaining scale is deleterious in several ways. Firstly, as already mentioned, it decreases heat transfer coefficient (Delgado et al., 1992; Müller-Steinhagen et al., 1994). Secondly, since sodalite scaling is controlled by chemical reactions (Addai-Mensah et al., 1998), it can be expected that the scaling rate will be higher on sodalite scaled tubes compared with a bare metallic surface, as was observed for gibbsite scaling of mild steel in pregnant Bayer liquor (Gavril et al., 2001). Finally, if undissolved sodalite scale is left on tube walls after an acid cleaning, after several cycles it will lead to the complete blockage of the heat exchanger tubes, as occasionally observed in the plants.

Analysis of a Blocked Heat Exchanger Tube

The picture shown in Fig. 7 shows the longitudinal cut of a blocked heat exchanger tube, in which banding of the Bayer sodalite is observed.

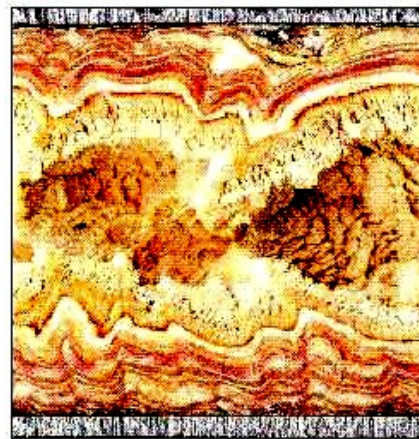


Fig. 7 Picture of a longitudinal cut of a heat exchanger tube blocked by sodalite (1.5×).

The banding has previously been observed for DSP scale and was associated with changes in the process (Roach, 1996). In the particular case studied here, the banding could be associated with acid cleanings where the sodalite scale was not completely dissolved.

The next figure is a micrograph of a small portion of the tube, including the mild steel wall.

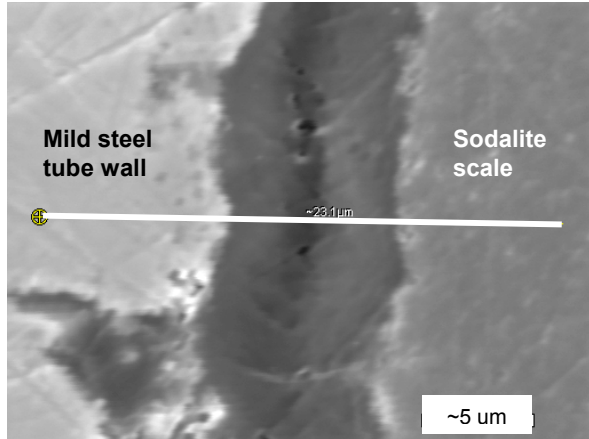


Fig. 8 Micrograph showing an area adjacent to the tube wall (the white line represents 23.1 μm).

In Fig. 8, three different areas are observed. An elemental analysis was done along the line shown in this figure which represents a thickness of 23 microns. Fig. 9 shows the results obtained from this analysis for six different elements: carbon, oxygen, sodium, aluminum, silicon and iron. The y-axis represents their relative concentration and the x-axis refers to the position on the 23 μm line in Fig. 8.

We can see that on the left side we have the tube wall consisting of iron, then follows a carbon layer of approximately 7-8 microns, followed by the sodalite scale where oxygen, sodium, aluminum and silicon are present.

This is very interesting since the same carbon layer is observed between every sodalite band. Fig. 10 shows a SEM photo of a scaled tube section and the area where an elemental mapping was done (presented in Fig. 11). This figure shows where the carbon is detected (pale lines). It can be observed that the carbon lines perfectly match the sodalite banding.

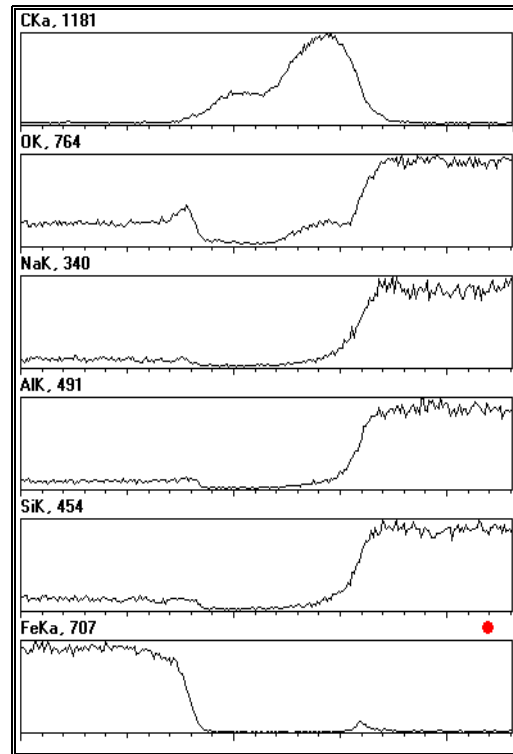


Fig. 9 Mapping of the elements present along the line shown in Fig. 8 (23 microns).

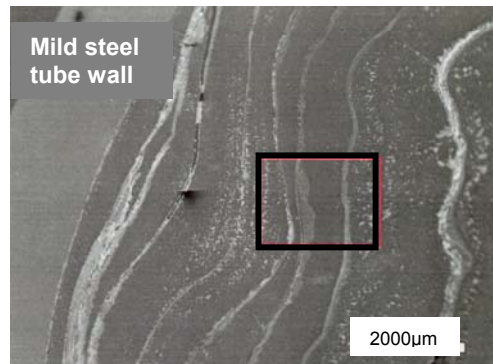


Fig. 10 SEM photo (15x) of a scaled tube section.

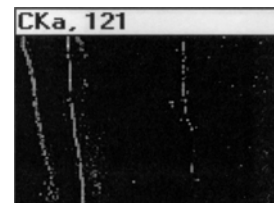


Fig. 11 Carbon content (pale lines) of the rectangular section of Fig. 10, determined by elemental analysis.

A possible hypothesis relative to the formation of a layer mostly composed of carbon is that a chemical reaction took place between the sodalite surface and the components of the corrosion inhibitor (mainly organic compounds). Such a reaction could also explain the results where the corrosion inhibitor prevents the total dissolution of the sodalite scale, since it could form an impervious layer on the sodalite surface.

Organic Additives to Sulfuric Acid Solution: Acetic Acid and Ethanol

It was reported in a Reynolds' patent that adding acetic acid (CH_3COOH) to diluted sulfuric acid solutions helps dissolving scale (Schmidt and Featherstone, 1969). This method was thus tested with and without a corrosion inhibitor. The results reported in Table 1 show that the addition of acetic acid effectively increases the percentage of scale that is dissolved at 70°C . Moreover, this improvement is much more significant when the corrosion inhibitor is present.

Table 1 Organic additives and dissolution efficiency at 70°C .

Solution	% of dissolution	
	No inhibitor	With an inhibitor
Sulfuric acid	> 95%	< 72%
Sulfuric and acetic acids	~99%	> 95%
Sulfuric acid and ethanol	> 95%	~80%

The authors of this patent were suggesting that the beneficial effect of acetic acid is attributed to the coordinating ability of acetate ions (CH_3COO^-) towards Al^{3+} that accelerates the dissolution of the aluminosilicate scale. The results shown in Table 1 suggest that it could also be due to its organic nature: hydrophobic interactions of acetic acid with the organic components of the corrosion inhibitor, preventing them from reacting with the scale surface (*c.f.* previous section).

The latter hypothesis was tested by adding ethanol ($\text{CH}_3\text{-CH}_2\text{-OH}$) to the sulfuric acid solution. Ethanol is an organic compound that is comparable, in size, to acetic acid, but with no complexing properties under these conditions.

Table 1 shows that even though ethanol has a positive effect on the dissolution percentage, its impact is not as important as the one of acetic acid. The increase from 72 to 80% when ethanol is added suggests, however, that the organic nature of the additive certainly plays a role towards

reducing the negative impact of the corrosion inhibitor on the scale dissolution. This is consistent with the hypothesis of a chemical reaction between the corrosion inhibitor and the sodalite scale surface that forms an impervious layer, preventing any further dissolution by sulfuric acid.

DISCUSSION

This fundamental study reproduces fairly closely what is observed in the plants. Effectively, the results suggest that even if the heat exchangers cleaning operations are well done, according to the established practice, scale could remain on tube walls if the temperature of the solution is too high. The most important consequence of this is the low heat transfer coefficient. In addition, tube blockages, occasionally observed in the plants, can be attributed to successive incomplete cleanings, a consequence of secondary reactions of the corrosion inhibitor with the sodalite surface, that leave a layer of undissolved scale onto which additional scale will form.

The fact that adding ethanol increases dissolution efficiency when a corrosion inhibitor is present is consistent with the idea of hydrophobic interactions between that kind of additive and the organic components of the corrosion inhibitor, preventing their reaction with sodalite scale surface. Ethanol is however not as effective as acetic acid in increasing the dissolution percentage at high temperatures. This suggests that acetic acid would act in two ways: preventing the corrosion inhibitor organic components to react with sodalite scale surface, and coordinative interactions with aluminum in the early steps of scale dissolution, that accelerate the sodalite dissolution process, as suggested in the Reynolds' patent (Schmidt and Featherstone, 1969).

CONCLUSIONS

The results obtained in the course of this research project have practical implications for the acid cleaning operations of heat exchanger tubes scaled with Bayer sodalite. It was shown that controlling the solution temperature is the key parameter to achieve a high dissolution efficiency during acid cleaning operations. Depending on the temperature, the presence of a corrosion inhibitor can play an important role in the sodalite scale dissolution with a sulfuric acid solution. It was shown that in presence of a corrosion inhibitor, the scale dissolution can stop before scale is completely removed, leading to tube blockages, and this phenomenon is more important as the temperature increases. SEM analyses have also shown the

banding of sodalite scale, likely resulting from these incomplete cleanings.

It was also observed that the addition of acetic acid could be beneficial to the sulfuric acid cleaning operation. Other ways to increase the scale dissolution rate are: increasing the flow rate, a higher acid concentration and a higher temperature. These parameters are useless, however, if the temperature is too high, since dissolution stops even sooner because of the presence of the corrosion inhibitor.

ACKNOWLEDGEMENT

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NOMENCLATURE

A	Frequency factor
E*	Activation energy
k	Kinetics rate constant
M_{start}	Total mass of the sample tube (tube + scale) at the beginning of the experiment
M_{end}	Mass of the sample tube at the end of the experiment
M_{scale}	Mass of scale contained in a typical sample tube
R	Perfect gas constant (8.3144 J/mol·K)
T	Temperature (K)

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