Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

THE IMPACT OF SULPHATE AND CARBONATE ON THE PERFORMANCE OF SILICONATE-TYPE POLYMERS AS INHIBITOR OF SCALING

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Keywords: aluminate liquor, evaporation, carbonate, sulphate, scale inhibitor, polymer, alumina

Abstract

The presence of sulfate and carbonate ions in the aluminate liquors results in the creation of scale on heat exchange surfaces during heating and evaporation. As inhibitor the liquid silicone polymers of siliconate type was used. Inhibitor is added directly into the substance. The effect of inhibitor concentration on the degree of sulfate and carbonate sediments encrustation of heat exchange surface of evaporator equipment was found. The results obtained in pilot and industrial conditions showed that with increasing concentration of inhibitor the speed of encrustation slows down. Complete cessation of encrustation achieved with the addition of inhibitor in the liquor is evaporated in amount of about 35 ppm. The results of using the inhibitor are expressed in steam consumption reduction for evaporation and grow capacity.

Introduction

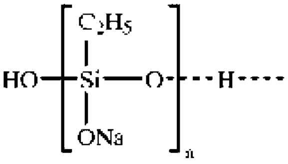
In the last decades the improving energy efficiency in leaching and evaporation in the processing of aluminium content raw materials to alumina is directed first of all to equipment component. Rising of process temperature is accompanied by intense precipitation on heat exchange surfaces of equipment newly formed solid phases whose solubility decreases with increasing of temperature.

When creating of new equipment designs for leaching and evaporation the preference given to those that allow for the circulation of technological liquors with high speed and, thus, to prevent scale.

Works on the selection and perfection of scaling inhibitors are conducted in two ways:
- creation of conditions preventing the growth of newly formed particles of the solid phase [1-4];
- creation of surface film on heat exchanger surface [5-8].

Evaporation of liquor in the processing of aluminum content raw material for alumina can be complicated by the intensity of scaling of sodium sulphate on the heat exchanger surface. Evaporation of aluminate liquors with sodium carbonate component may also lead to the isolation process, i.e. soda deposition on heat exchange surfaces in the form of scale, creating thermal resistance. This limits the performance of evaporation and leads to the need for equipment cleaning.

As inhibitor silicon-oxigen polymer with ethyl and-ONa group attached to the silicons was studied, i.e.



$$HO-\left[\overset{C_2H_5}{\underset{ONa}{Si}}-O-\right]_n\cdots H\cdots$$

Sodium ethylsiliconate $C_2H_5Si(OH)_2ONa$ is obtained by hydrolysis of $C_2H_5SiCl_3$ with followed dissolution of the hydrolysis products in aqueous-alcoholic solution of alkali. This fluid is alkaline (pH 13-14), 1,17-1,21 g/cm^3 density, highly soluble in water and ethyl alcohol, using no harmful vapors and gases.

This water repellent organic silicon fluid that has brand GKJ-10, which can be considered as a liquor of the polymer or the product of its interaction with the aluminate liquor.

Water-soluble silicone salts (as used here sodium ethylsiliconate) are highly alkaline liquors containing 20-30% siliconates. This is a random salt, but water-repellent films, when dry, are probably already polymers and therefore it is possible to consider these substances as polymer liquors. On this basis in highly alcaline medium they are soluble and can be used to create a liquid film on the heat exchanger surfaces leading to a decrease of adhesion at the liquid-solid, straight into the aluminate liquor.

Tested inhibitor of siliconate type creates a liquid film on heat exchanger surface which is the barrier to lasting consolidation of scale on the heat exchange surface [5-8].

Inhibitor of siliconate type is suitable for heat exchange surface protection against silicon deposits [8].

Experimental

Research were conducted to determine the fundamental possibility of siliconate type scaling inhibitor of application for slowing down of scale formation at evaporation of sulphate content aluminate liquors.

Investigations were carried out on the model of the evaporator with natural circulation and the heat transfer surface of 2,4 m^2. Boiler unit consisted of three steel heat exchange tubes 57 x 3.5 mm and a length of 5 m rigidly fixed to the tube sheets. Before each experiment, the inner surfaces of the tubes were treated with 10 % HCl. Before the experiment and after the experiment apparatus was opened and made a visual inspection of the heat exchange surface by radiographic analysis of each tube. Washing of contaminated heat exchange surface of the sulphate scale was performed with hot water.

Inhibitor effect on the kinetics of heat transfer surfaces inlaying was determined by the change in the heat transfer coefficient (K) in time. It was calculated by the formula

$$K = \frac{Q}{F \cdot \Delta t}$$

where Q - energy transferred as heat; F - heat exchange surface; Δt-useful temperature difference.

Transmitted energy as heat Q is determined from the mass and energy balance of the interacting flows to evaporator

$$Q = g\,(i - C_W \cdot t),$$

where t - temperature of the liquor; g - fuel vapor; C_W - heat of water; i - enthalpy of vapor.

When this assumption is made that the liquor temperature at the input and output of the unit are approximately equal. This assumption underestimates the true K by evaporation (about 10%). However, this assumption is justified as determined by the relative change in K.

Concentration GKJ-10 adopted 1 g/l. In the experiments was used the aluminate liquor containing, g/l: R_2Ototal – 128 (where R_2O is sum Na_2O+K_2O as Na_2O); R_2Ocaustic – 118; Al_2O_3 - 54; K_2O – 46; SO_3 - 41,4. The aluminate liquor was evaporated to concentration 200-220 g/l of R_2Ocaustic.

Evaporator has been working in the following conditions:

Boiling-point of aluminate liquor, °C	112-113
Useful temperature difference, degree	20
Consumption of initial liquor, l/hour	180
Temperature of liquor after preheating, °C	107
Density of initial liquor, g/dm^3	1,21
Density of strong liquor, g/dm^3	1,34-1,35

Results and discussion

Duration of the experiment without inhibitor was 12 hours. During this time coefficient K decreased from 1000 to 460 W/(m^2·degree) that indicates the intensity of the heat exchange surface overgrown by sulphate scale. Change of K is represented as function of time in Fig. 1.

From Fig. 1 follows that in the absence of inhibitor (curve 1), the value of K decreases sharply. In this case, a visual inspection showed a heat exchange surface that at the evaporator tubes present scale layer thickness of 1.5-3.0 mm; the pellet surface is uneven; the adhesion of scale to metallic surfaces is high. On the inner surface of tubes found a thin layer of silicone (sodium ethylsiliconate).

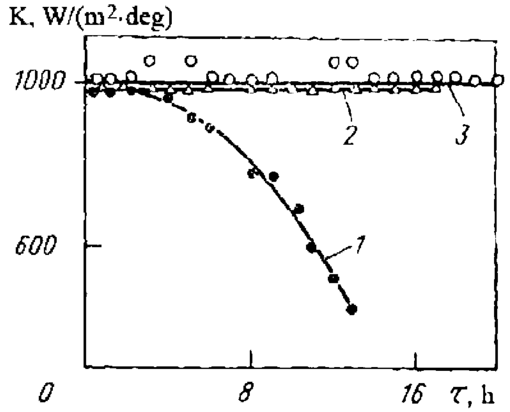


Figure 1. Dependence of the heat transfer coefficient (*K*) by evaporation of sulfate content aluminate liquors on the duration of experiment (τ):
1 - evaporator operation without inhibitor;
2 - evaporator operation with the inhibitor for 17 hours;
3 - evaporator operation with the inhibitor for 47 hours

In presence of inhibitor (curves 2,3) in liquor in quantity 300 ppm as dry substance and if the duration of the evaporation 17 and 47 hours the significant reduction in K was not observed. Visual inspection of the heat transfer surface after experiments with the inhibitor of scaling revealed that the internal heat exchange surface is clean. Suitability of K in time as well as the results of visual inspection of the interior heat exchange surface allows us to conclude on the prevention of scale formation in evaporation aluminate liquor in the presence of inhibitor.

Subsequent investigations directed to optimization of inhibitor concentrations made it clear that positive results may be reached when added less than 30 ppm of the inhibitor.

Evaporation of aluminate liquors with sodium carbonate component

Experiments were carried out to determine the effect of the scaling inhibitor on kinetics of sodium residues formation at evaporation heat exchange surface. To pilot plant experiment the aluminate liquor was prepared in which, g/l: Na_2Ototal – 214; Na_2Ocaustic – 187; Al_2O_3 - 88. The aluminate liquor was evaporated to concentration 300 g/l of Na_2Ocaustic.

The influence of the concentration of the inhibitor on the value of thermal resistance (the inverse of K) was studied. The concentration of the GKJ-10 inhibitor was varied in the range of 0 ÷ 100 mg/l. Evaporator has been working in next condition: boiling-point of aluminate liquor117-119 °C; useful temperature difference 12-15 degrees; duration of evaporation 24 hour.

Analysis of experimental data (Fig. 2) led to come to conclusion that with increasing concentration of the inhibitor effect on scaling increases as well.

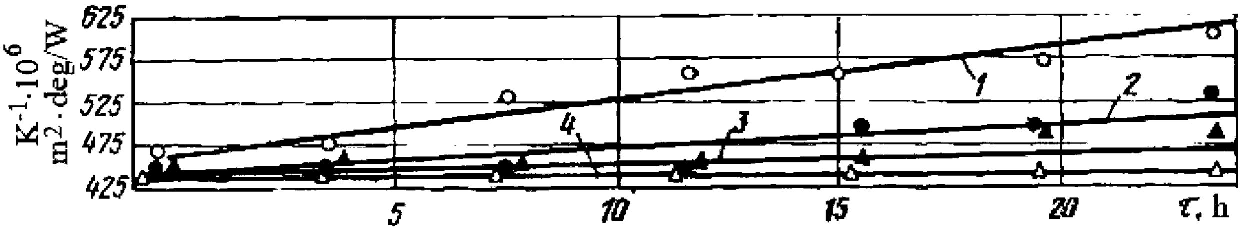


Figure 2. Effect of concentration of inhibitor on thermal resistance by evaporation at GKJ-10 inhibitor concentration in mg/l: 1 – 0; 2 – 10; 3 – 50; 4 - 100.

Investigations of the kinetics of scaling have allow establishing that changes in the coefficient of thermal resistance over time are approximated by straight lines with different angles of inclination. The greatest increase in the coefficient of thermal resistance on transfer surfaces was noted in the absence of scaling inhibitor. In the presence of the inhibitor the coefficient of thermal resistance was increased to the lesser extent, at GKJ-10 inhibitor concentration 100 mg/l (30 ppm in recalculation on dry substance) the complete prevention of scale formation occurred.

The obtained data were also checked in industrial conditions at concentration of scale formation inhibitor 10 mg/l (3 ppm in recalculation on dry substance) on the operating evaporating train. The obtained results confirm improvement of the main regime and operational indicators of the train work: the slowed-down incrustation of boilers of the evaporating devices, steady concentration and thermal mode when receiving evaporated liquor with higher concentration, processes of transfer of energy in the form of heat were characterized by higher rates of a heat transfer on cases of evaporating devices. When using inhibitor the termination of foaming of liquor in evaporating devices was noted. Generally, industrial train test results corresponded with tests semi-works. Thus, for 24 hours of the plant experiment at 10 mg/l of GKJ-10 inhibitor in the liquor, scale formation in evaporation train decreased two and half times.

Conclusion

The studies of the effect of siliconate liquid polymers additives on heat transfer surface scale intensity by sulfates and carbonate residues have shown that the addition of this inhibitor in aluminate liquor retards or prevents incrustation processes of heat exchange surfaces. Addition of the inhibitor in an amount of less than 35 ppm calculated as dry substance fully blocked this process. The results obtained for a wide range of scale-forming components allow predicting the success of the application of siliconate type scaling inhibitor during heating and evaporation of bauxite slurries of alumina production.

References

1. J. Addai-Mensah A. R. Gerson, K. Zheng, A. O'Dea, and R. St.C. Smart, "The precipitation mechanism of sodium aluminosilicate scale in Bayer plants", Light Metals 1997 (Edited by R. Huglen, The Minerals, Metals & Material Society, 1997), 23-28.

2. J. Addai-Mensah, J. Li, M. Zbik and W. Wilmarth, "Microstructure and uranium adsorption behaviors of sodium aluminosilicate polytypic in caustic aluminate liquors" Light Metals 2005 (Edited by Halvor Kvande, The Minerals, Metals & Materials Society, 2005), 171-176.

3. D. P. Spitzer, A. S. Rothenberg, H. I. Heitner, F. Kula, M. Lewellyn, "Reagents for the elimination of sodalite scaling", Light Metals 2005 (Edited by Halvor Kvande, The Minerals, Metals & Materials Society, 2005), 183-188.

4. D. P. Spitzer, Q. Chamberlain, C. Franz, M. Lewellyn, and Qi Dai, "MAX HT^{TM} sodalite scale inhibitor: plant experience and impact on the process", Light Metals 2008 (Edited by David H. De Young, The Minerals, Metals & Materials Society, 2008), 57-62.

5. V. G. Kazakov, and G. A. Kazakov, Patent USSR 500,290, 30.09.1975.

6. V. G. Kazakov, N .G. Potapov, and A. E.Bobrov, "Intensification of sodium-alkaline aluminate liquors evaporation", Tsvetnye Metally, (6)(1978), 40-42.

7. V. G. Kazakov, and N. G. Potapov, "Use of an Organosilicone Inhibitor in the Evaporation Step of Aluminate Liquors", Tsvetnye Metally, (8) (1982), 39-41.

8. V. G. Kazakov, and V. A. Lipin, "Using of siliconate-type polymers as inhibitor of scaling at aluminate liquors heating and evaporation", Light Metals 2014 (Edited by John Grandfield, The Minerals, Metals & Material Society, 2014), 73-76.