# USING OF SILICONATE-TYPE POLYMERS AS INHIBITOR OF SCALING AT ALUMINATE LIQUORS HEATING AND EVAPORATION

Vladimir G. Kazakov<sup>1</sup>, Vadim A. Lipin<sup>2</sup> <sup>1</sup>St. Petersburg State Technologic University of Plant Polymers 4, Ivana Shernykh st., St. Petersburg, 198095, Russia <sup>2</sup>St. Petersburg State Polytechnical University 29, Polytechnicheskaya st., St. Petersburg, 195251, Russia

Keywords: aluminate liquor, evaporation, desilication, scale inhibitor, polymer, alumina

### Abstract

At heating and evaporation of aluminate liquors the liquid organic silicon polymers of siliconate type were used. This type of material is characterized by antiadhesive properties and at sufficient surplus of polymer, can cover an inside wall of the heat exchange tubes with a thin layer on which the sodalite is less likely to stick. This reagent can greatly reduce or even completely eliminate sodalite scaling in heat exchangers, pipes, etc. what are confirmed in pilot plant, and plant tests. Obtained positive data at heating and vaporization of high silica liquors at presence of 50-100 mg/l (15-30 ppm to dry substance) scale inhibitor allow concluding about an opportunity of heating and vaporization these liquors in heat exchangers of recuperative type. The result of use of the inhibitor is expressed in decrease in the charge of vapor to the evaporation and increase in its throughput.

### 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 scale prevent.

However, the direction associated with the prevention of precipitation or scale formation on basis of inhibitors has not been given enough attention.

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 [5-7].

In the processes of leaching and evaporation on heating surfaces crystallized sediment-components. Emerging crystals firmly adhere to the uneven surface micro-roughness and heat forming a thin film of scale. The presence of the heating surface microroughness creates favorable conditions for nucleation and crystal growth.

One of the most important tasks for improving the surface heat flux at the thermal processing of aluminate liquors during leaching of bauxite, evaporation of the mother liquor or desiliconization of aluminate liquor is to slow or prevent the heating surface inlaying by sodium hydroaluminosilicate, soda or sulphate-soda precipitations.

Max HT scaling inhibitor of Sytec reduces scale formation in evaporation and heating aluminate liquors [3,4]. The mechanism of action of this inhibitor is based on the blocking of crystal components of the liquor, i.e. suppression of crystallization.

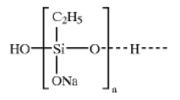
According to the information the addition to aluminate liquors of Max HT inhibitor (evaporation and autoclave leaching) led to some plants to slow of scale formation rate in 2.5 -3 times when inhibitor concentration 30-100 mg/l (25-30 ppm). In some cases, this effect was not observed. Fully prevent scale formation is not established when used doses or by evaporation or by autoclave leaching of bauxite.

Tested inhibitor of siliconate-type acts differently [5-7]. It creates a liquid film on heat exchanger surface which is the barrier to lasting consolidation of scale on the heat exchange surface.

## Selection and description of using inhibitor

If a clean surface of heat exchanger to protect by grease layer with a low work of adhesion it will significantly reduce the intermolecular bonds of crystals forming from liquor with heat exchange surface.

The suitable material for this purpose is silicon-oxigen polymer with ethyl and –ONa group attached to the silicons, i.e.



Sodium ethylsiliconate  $C_2H_5Si(OH)_2ONa$  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<sup>3</sup> 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 [5-7].

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 drugs as polymer solutions. On this basis in highly alcalisches 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.

Sodium poly-silicon-alkyls are well combined with alkaline solutions and create on surface of heat exchange the liquid volatile silicone unadhesion film. The crystallization of scale is the usual way, but it does not crystallize on heat exchanger surface micro-roughness. This process takes pace at the hydrophobic liquid film.

Thus organic silicon fluid is adsorbed on the surface of the heat exchanger and prevents the free penetration of the crystal to the heat exchanger surface.

Analysis of physical and chemical properties of surfactants in general and silicone liquid polymers in particular, leads to the conclusion that a significant slowdown of heat exchanger surfaces incrustation can be achieved by joint action in sufficient excess aluminate liquor of silicone liquid polymer GKJ-10, and the flow rate.

The important advantage of this method is the lack of influence on crystallization of scale with the addition of sodium poly-alkylsiliconate in liquor. Otherwise, this effect may lead to negative consequences in evaporation of liquors with the precipitation of large amounts of the solid phase.

Addition of the liquid organic silicon polymer in liquor will not only reduce heat exchanger surfaces scale in process of aluminate liquor concentration, but also intensify the processes of heat exchanger in general. The positive effect is observed when adding GKJ-10 in condensing steam. Hydrophobization of surface leads to a significant intensification of the process of heat exchanger from the condensing steam by moving film condensation to drip. Decrease in the specific surface free energy of solution with the addition of it GKJ-10 leads to the enhancement of heat exchanger.

Evaporation of aluminate liquors, rich in organic compounds, often entails foam, which creates serious difficulties. It is known that silicone are helpful defoamers, and the destruction of the foam is achieved at very low levels of silicone.

Polyetilsiliconate liquids also have good lubricity. Therefore, they, apparently, can be used not only as an anti-adhesion agent, but also as anti-corrosion.

Thus the addition of GKJ-10 in the solution solves problems intensification of heat exchanger and offers the prospect of simultaneously improving several chemical and technological parameters.

### Experiments on evaporated of aluminate liquors

In heat treatment processes of aluminate liquors namely in the processes of evaporation, desilication, autoclave leaching should to remove from surface of heat exchangers of scale that forms based on sodium hydroalumosilicate which has mainly sodalite structure. This scale has a very high bond strength to the heat exchange surface.

Experiments were fulfilling to slow of scaling speed these sediments by using of liquid organic silicon polymer GKJ - 10.

Investigations were carried out on a semi-industrial model of evaporator with forced circulation. Circulation speed was 1.5 m/s.

In the experiments, aluminate liquor of the following content, g/l:  $A1_2O_3 - 105,6$ ; NaOH as Na<sub>2</sub>O - 122,0; Na<sub>2</sub>CO<sub>3</sub> as Na<sub>2</sub>O - 16,0; SiO<sub>2</sub> - 2,2 was used.

Basic operational parameters of the process are:

- concentration of caustic alkali (NaOH as Na<sub>2</sub>O) in a strong liquor 196 g/l;
- heating vapor temperature 132 °C;
- useful temperature difference of 22 °C;
- atmospheric pressure.

The duration of experiments was chosen from the condition of plating thickness of scale on the heat exchange surface 0.3 - 0.5 mm. This plating thickness is operational acceptable in terms of it removal by chemical methods and to provide the required performance of evaporator. The scale obtained in the control experiment in 35 hours. In this case, the heat exchanger coefficient decreased by half. This duration took place in all the experiments with inhibitor of scaling. To determine of effect of inhibitor concentration on the kinetics of scale formation inlaying of exchange surface the evaporation was carried out at different inhibitor concentrations: 10, 50, 100 mg/l. Slowing effect was determined by the change in the reciprocal of the heat exchanger coefficient (K•10<sup>-6</sup>)<sup>-1</sup>, m<sup>2</sup>•deg/W.

## Discussion of the results for the evaporation

Analysis of experimental data (fig. 1) suggests that the change in the reciprocal of the heat exchanger coefficient  $(K \cdot 10^{-6})^{-1}$  at variable concentration and time during evaporation of high-siliceous aluminate liquors in the presence of liquid organic silicon polymer indicates slower scaling. Slowing effect of scale formation increases with increasing concentration of GKJ-10 and when the inhibitor concentration scaling of 100 mg/l (30 ppm) scale formation on the heat exchange surface is prevented completely.

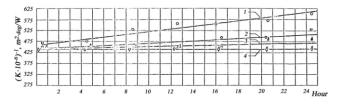


Fig.1 Kinetics of inlaying one heat exchanger surface during evaporation at inhibitor concentrations: 1- absence; 2 -10, 3 - 50, 4 - 100 mg/l.

Visual inspection of the evaporator tubes showed that the scale in experiments with inhibitor of scale formation was loose, not firmly bound to the surface. In control experiments without inhibitor derived scale characterized by firmness, solid structure and very high adhesion to metal heat exchanger surface.

## Experimental on heating aluminate liquors

The of heat exchanger surface inlaying process hydroaluminosilicates sodium (sodalite) during heating of aluminate liquor has its own characteristics compared to evaporation. This is due to the solubility of silica in these liquors namely with increasing concentration of aluminate liquor solubility of silica increases. Therefore, the heating process to highly aluminate liquor must occur in more strong conditions from the point of scaling (no compensating increase in concentration of aluminate liquor, as is the case during evaporation). The experiments were conducted on a model of a

vapor-liquid heat exchanger of shell and tube type with heat exchanger surface  $1.1 \text{ m}^2$ . The speed of the liquor circulating in the heat exchanger is 1.5 m/s.

In the experiments, aluminate liquor of the following content, g/l:  $A1_2O_3 - 140,0$ ; NaOH as  $Na_2O - 140,0$ ;  $Na_2CO_3$  as  $Na_2O - 4,0$ ;  $SiO_2 - 3,5 \div 4,0$ .

## Discussion of the results of the heating

Experimentally found (fig.2) that for 44 hours of work due to fouling of heat exchanger surface the heat exchanger coefficient of down from 1150 to 830 W/m<sup>2</sup>·degrees. Introduction to crystallizing a liquor of 50 mg of the inhibitor (concentration selected from studies in evaporation of high-silicon aluminate liquor) allowed to work without a visible reduction of heat exchanger coefficient 176 hours. The constancy of the heat exchange surface revealed that heating the liquor to highly able to hold without scaling.

Some variation in the numerical values of the heat exchange coefficient in time associated with fluctuations in other variables, namely the performance of plant by the initial liquor (V, l/hours), the liquor temperature at the inlet to the heater (T, K), the difference between temperature of vapor and heated liquor ( $\delta t$ , degree), the difference between temperature of heated liquor and the initial solution ( $\Delta t$ , degree).

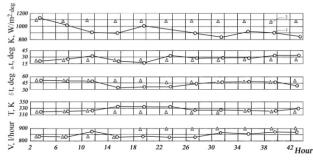


Fig.2 Changes in heating mode parameters to highly aluminate liquor at inhibitor concentrations: 1- absence; 2 - 50 mg/l.

### **Conclusions and recommendations**

The positive data on heating and evaporation of high-silica liquor in the presence of 50-100 mg/l (15-30 ppm) inhibitor of scaling allow us to conclude about the possibility of heating and evaporation of high-silicon aluminate liquors in the recuperative heat exchanger.

Currently heating of pulp for option hardware and technological scheme of one of Russian alumina plants are in fast vapor-pulp heat exchanger to a temperature of 130 -150 °C, followed by heating in autoclave to temperature of 230-235 °C with direct steam of thermoelectric plant. Limitation of regenerative temperature is the result of intense scaling of heat exchanger surface by precipitation of a complex chemical and mineralogical composition. Solving this problem will reduce of vapor consumption for bauxite autoclave leaching only on 1,5-6 times. The first number corresponds to the achievement of regenerative temperature of 180 °C to 150 °C at the present time during multistage self-evaporation of pulp. The second number corresponds to

the achievement of regenerative temperature of pulp 220 °C during pulp-pulp heat. Compared to the option of adopting the reaction temperature is 235 °C. Thus, the consumption of heat in the pressure leaching of bauxite 1.2 Gcal/t of alumina the consumption of heat from an external source can be reduced to 0.8 - 0.2 Gcal/t of alumina. Effect of reducing the flow of heat from an external source is equal to 0.4-1.0 Gcal/t of alumina.

Additional benefits include:

- 1. Entering of steam in autoclaves virtually eliminated due to the high temperature of regenerative pulp. While maintaining the concentration of caustic alkali in the reaction it allows to increase productivity of the autoclave battery.
- 2. Reduces the consumption of vapor from thermoelectric plant and increases throughput of evaporation since the cycle is closed at the lower concentrations of alkali.
- 3. Addition of scaling inhibitor in evaporation increases the performance of the evaporator battery.

Inhibitor of siliconate-type brand GKJ-10 in the tests showed high efficiency of up to fully prevent scale formation at its concentration of 100 mg/l (30 ppm). If necessary, this concentration can be changed considering the cost of inhibitor and received positive effect. There are also improved chemical and technological parameters with the addition of the inhibitor in aluminate liquors namely sedimentation properties of the red mud, increasing the heat exchanger coefficient on clean heat exchanger surfaces, etc.

## Conclusion

The effect of surfactant on the degree of fouling of heat exchange surfaces by encrusted sediment on the example of water-repellent organic silicon fluid of siliconate-type (GKJ-10) was investigated. It is shown that the introduction of GKJ-10 dramatically reduce of heat exchange surface scale. The intensity of overgrowth of heat exchange surface slows down, and in the limit (when adding GKJ-10 in the liquor in an amount of 100 mg/l (30 ppm to dry substance), totally prevented.

Inhibitor of siliconate-type by the example of sodium ethylsiliconate (GKJ-10):

- No negative effect on the chemical and technological process;
- Contributes to the intensification of heat exchanger process;
- Has the effect of corrosion;
- Prevents foam during evaporation of aluminate liquors.

### References

- 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", <u>Light Metals 1997</u> (Edited by R. Huglen, The Minerals, Metals & Material Society, 1997), 23-28.
- J. Addai-Mensah, J. Li, M. Zbik and W. Wilmarth, "Microstructure and uranium adsorption behaviors of sodium aluminosilicate polytypic in caustic aluminate liquors" <u>Light Metals 2005</u> (Edited by Halvor Kvande, The Minerals, Metals & Materials Society, 2005), 171-176.

- D. P. Spitzer, A. S. Rothenberg, H. I. Heitner, F. Kula, M. Lewellyn, "Reagents for the elimination of sodalite scaling", <u>Light Metals 2005</u> (Edited by Halvor Kvande, The Minerals, Metals & Materials Society, 2005), 183-188.
- D. P. Spitzer, Q. Chamberlain, C. Franz, M. Lewellyn, and Qi Dai, "MAX HT<sup>TM</sup> sodalite scale inhibitor: plant experience and impact on the process", <u>Light Metals 2008</u> (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.
- V. G. Kazakov, N.G. Potapov, and A. E.Bobrov, "Heating and Evaporation of Silica-containing Aluminate Liquors", Tsvetnye Metally, (10)(1979), 45-48.
- 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.