

EFFECT OF ACID CLEANING USING INHIBITOR IN A TUBULAR DIGESTION AND IN A VAPOR RECOMPRESSION EVAPORATOR AT SUMITOMO'S ALUMINA REFINERY

Ogawa, T¹, Nishimura, A¹, Sasaki, H², Ishida, T², Harato, T^{2*}

¹ Sumitomo Chemical, Ehime, Japan

² Asahi Chemical, Osaka, Japan

Abstract

It is very important to keep the heat transfer surface clean to operate the Bayer circuit steadily with low energy consumption. This paper will outline the chemical cleaning of a tubular digester and a falling film evaporator with vapor recompression system which was developed by Sumitomo group.

1. When calcium compounds are added in a digestion step to remove organic compounds and to causticize the liquor, Ca-contained sodalite is formed. The scale is difficult to clean chemically by H₂SO₄ because of insoluble CaSO₄ on the scale during acid cleaning. An inhibitor for HCl cleaning was developed and applied to Sumitomo's low temperature tubular digester. The equipment material (low carbon steel) is sound after a few hundreds times cleaning.
2. We developed a falling film evaporator with vapor recompression system. Evaporated vapor is recompressed by electric compressor and used as vaporization steam. In this vaporization system, vapor is not exhausted into cooling water as in a conventional multi-stage flash evaporator. Thus the energy consumption is very low compared to a conventional one. As for scaling on the heat transfer surface, after searching for the optimum operation conditions, we clean it chemically using corrosion inhibitor every six month to keep a heat transfer coefficient of 3,000–4,000 J/m²·sec·K. In our plant (60 t/hr) actual energy consumption per ton of water is (0.002t-steam + 37Kw-electric power). It is about 1/5–1/6 of a multi-stage flash evaporator.

1 Introduction

The global environmental problem is a big issue to be solved in the beginning of this century. Scale deposited on the heat transfer surface decrease the heat transfer coefficient, resulting in increased energy consumption, higher labor demand, costly cleaning program and loss of productivity.

There are many studies on desilication and scale-forming reactions. There are some investigations that aluminosilicate scale on Bayer plant heat exchangers is reduced by selective seeding and use of some additives (Mensah, 2001).

A limited number of studies of chemical cleaning by adding corrosion inhibitor to minimize corrosion damage of equipment material have been published (Fortin, 2003).

Many kinds of scale are formed in the evaporation step, but there is no investigation on the depression of scaling based on the characteristics of evaporator and the recovery of heat transfer efficiency by chemical cleaning.

Falling film evaporator which shows very high heat transfer coefficient is applied to alumina refinery (Ainscow, 2002), but there is no indication on the reduction methods of scaling and heat transfer efficiency.

This paper will outline the chemical cleaning of a tubular digester and a falling film evaporator with vapor recompression system which was developed by Sumitomo group.

It also reports on the low energy consumption of a vapor recompressive evaporator compared to a multi-stage evaporator and on the scale depression conditions.

2 Digestion process

2.1 Digestion process at Sumitomo

Sumitomo produced alumina from Gibbsite and Boehmitic bauxites in the past. Gibbsite bauxite was digested at low temperature (150°C) by a series of tubular reactors and Boehmitic bauxite was digested at high temperature (220°C) by a series of autoclaves. Sumitomo stopped the production of SGA and shifted to specialty alumina during the second oil crisis of 1980s. Then one low temperature tubular digestion train was left. A caustic saving process was developed in 1993 and operated for about seven years. But it was converted to a conventional tubular digestion process in 2000, because the scaling in a pressure decanter caused a bottleneck for increasing production rate of chemical alumina.

This section will describe the chemical cleaning of Ca-contained sodalite¹ scaled on the tubular digester.

2.2 Digestion conditions and characteristics of scale

Block diagram of the digestion process is shown in Figure 1. Bauxite slurry and strong liquor are put together and then passes to a series of tubular digesters. The mixed slurry passes the center tube and is heated to 150°C by flashed and live steam, and then goes to a desilication tank. The desilicated slurry is cooled through three stages of flash tanks and then passes to a BR settler. Slaked lime is added at the entrance of digestion to remove some organics and to causticize the liquor by about 0.4% (as CaO/bauxite).

¹ Many forms of aluminosilicate precipitate in the Bayer liquor. Hereinafter they are referred to as "sodalite" except as otherwise noted.

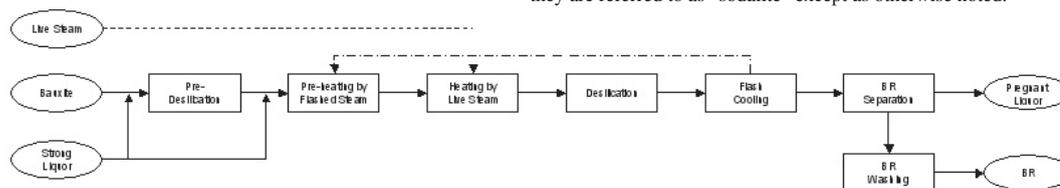


Figure 1 Schematic Diagram of Digestion Stage

The digestion conditions (before flash cooling) are

C-Na ₂ O, g/l	125
Al ₂ O ₃ , g/l	152
M.R., -	1.35
Digestion Temperature, °C	150
Velocity of Slurry, m/sec	2.0–2.5

Scaling reaches a maximum at the end of digestion tube where the slurry is heated to the highest temperature.

Table 1 shows the analysis results of the scale sampled at the end of the digester. The main components were natrodavynite (3NaAlSiO₄·Na₂CO₃) and hematite (Fe₂O₃). About 1% of calcium was detected by chemical analysis, but the crystal form was not determined by X-ray analysis. We guess it must be Ca substituted cancrinite (Duncan, 1996).

Table 1 Analysis of Scale inside the Final Digestion Tube

Operation Temperature, °C		150
Operation Days, days		41
Component	3NaAlSiO ₄ · Na ₂ CO ₃	main
	Al ₂ O ₃ · 3H ₂ O	-
	Al ₂ O ₃ · H ₂ O	-
	Hematite	main
	Goethite	sub
	Unknown	detected
	Ca(Chemical Analysis), %	1.0

2.3 Laboratory acid cleaning test

When we started the low temperature tubular digestion process adding lime, the scale was chemically washed by H₂SO₄. It was difficult to make the heat transfer surface clean enough to recover from the formation of insoluble calcium sulfate on the scale surface by the reaction of calcium compound and H₂SO₄. Then we ran a series of tests on the dissolution of the scale by H₂SO₄ and HCl with/without corrosion inhibitors.

Test procedure and conditions are

■ Procedure

- 1) Same size of scale in a plastic net was suspended in a 500 ml beaker with an agitator(250 rpm)
- 2) Acid was poured into the beaker kept at 50°C
- 3) Weight change of the scale was measured

■ Acid

- HCl, g/l 110
- H₂SO₄, g/l 150

■ Corrosion Inhibitor²

- For HCl: IBIT 2S, % 0.5
- For H₂SO₄: IBIT 50SR, % 0.5

■ Material of equipment

- STPG

The measured dissolution rate of the scale is shown in Figure 2.

Figure 3 shows the corrosion rate of the material.

It is clear that Ca-contained sodalite was rapidly dissolved by HCl compared to H₂SO₄. Figure 2 also shows that IBIT 2S does not hinder the dissolution of scale as Fortin (2003) indicated that the presence of corrosion inhibitor reduces the efficiency of the cleaning operation at high temperatures.

Corrosion rate of 2.8 mm/Y corresponds to the low corrosion of 0.2mm by the repeated 300 times of chemical cleaning of each 2 hours, ten times a year and for thirty years.

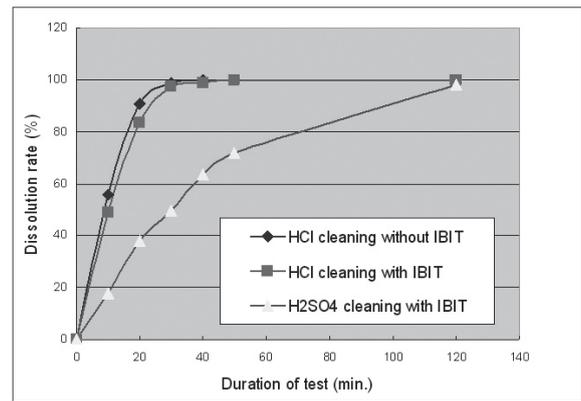


Figure 2 Dissolution Rate of Ca-contained Sodalite by Acid

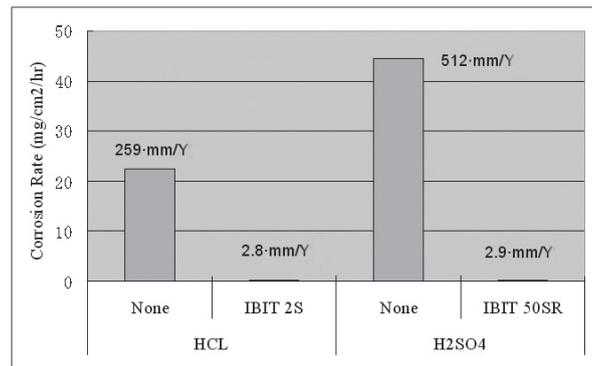


Figure 3 Corrosion Rate of material with/without IBIT

2.4 Acid cleaning of the plant

A tubular digester separated from the train is chemically cleaned by circulating HCl. Cleaning conditions are:

- HCl, m³ 35
- Initial concentration, g/l 110
- Temperature, °C 50
- Velocity of circulating acid, m/sec 0.8–1.2
- Circulation time, hr 1.5–2.0

Figure 4 shows the change of heat transfer coefficient (U) of the last stage digester. By the HCl cleaning it is recovered to about 1600 J/m²·sec·K and then reduces to 800–1000 J/m²·sec·K for about 40 days operation. The equipment material has been perfectly sound after a few hundreds times of cleaning since the start up of the equipment.

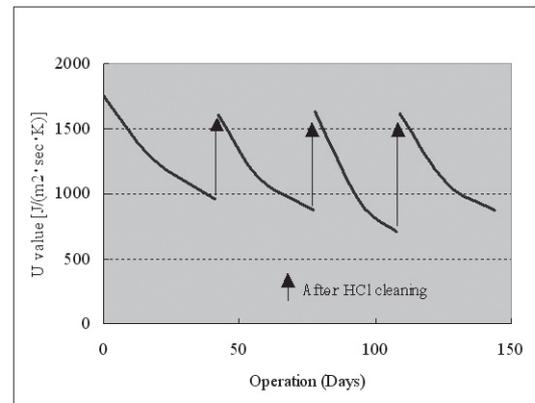


Figure 4 Change of Heat Transfer Coefficient (U) of Tubular Digester (Live Steam Heating Section)

² "IBIT" is a trade name of corrosion inhibitor developed by Asahi Chemical. These inhibitors are designed for alumina refinery.

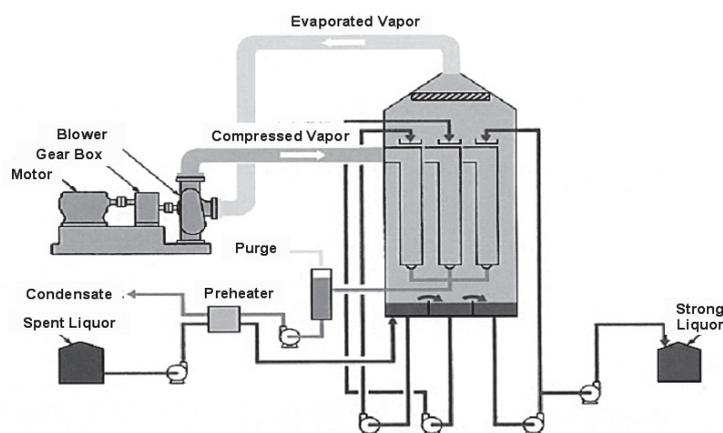


Figure 5 Schematic Diagram of VRCE (3 evaporation sections are shown)

3 Evaporator

When Sumitomo left one low temperature digestion train using Gibbsite bauxite, it required to increase the evaporation capacity to maintain the water balance because the specialty hydrate required a large quantity of water for washing hydrate.

In the selection of an evaporator we have to consider three major factors: (1) running cost (mainly utility steam and electric power), (2) initial cost and (3) maintenance cost. We adopted a vapor re-compressive evaporator (VRCE) after the examination of VRCE and multi-stage flash evaporator and pilot test of VRCE, mainly from the view point of low energy consumption.

In order to maximize the merit of VRCE, it is essential to keep the heat transfer coefficient as high as possible. This means that it is very important to keep the heat transfer surface as clean as possible.

3.1 Description of vapor re-compressive evaporator (VRCE)

Schematic flow of VRCE is shown in Figure 5. We decided the operation conditions and details of equipment after pilot test (Ishida, 1993).

Spent liquor is heated to 80°C and passes to the first evaporation section in the VRCE which is composed of four evaporation sections in a body (three sections are shown in the figure). The liquor circulates through the falling film evaporator. As the liquor flows down through the plate it is heated by the re-compressed vapor which condenses inside the plate and goes to the sump.

The liquor becomes progressively more concentrated as it passes through the units. Finally it is discharged from the fourth section. The vapor leaving the evaporator passes through an internal demister and then enters a blower where it is adiabatically compressed. The compressed and heated vapor is used as a source of heat for all evaporator sections.

In a multistage evaporator, vapor from the coldest effect is difficult to reuse and generally accompanied by cooling water. Only condensate is the heat discharged from VRCE except heat loss (the condensate is used for washing hydrate). This is the reason why energy consumption of VRCE is so low.

The enthalpy of the re-compressed vapor depends on the performance of blower. When a conventional blower is applied the temperature rise of vapor is around 10°C. Then the temperature difference of vapor and liquor is so small as 5°C because of BPR of the liquor. Heat transfer coefficient of clean plate is 4000–5000 J/m²·sec·K. In order to reduce the initial cost and to take advantage of energy efficiency (use small temperature difference), it is very important to keep the heat transfer coefficient as high as possible. In other words, it is very important to establish the operation conditions avoid scaling, and to establish the easy cleaning method for the deposited scale.

3.2 Scaling in the VRCE and cleaning methods

Scaling occurs when through a temperature or concentration change the saturation level is exceeded and a solid phase precipitates out of the solution. Three scales of sodalite, sodium phosphate and sodium fluoride are generally generated at evaporation stage. Here tendency

for scale formation in VRCE is discussed compared to a multistage evaporator and the de-scaling policy is decided.

■ Sodalite scale

Sodalite scales out at every stage of Bayer circuit. Though the content of SiO₂ in spent liquor is low compared to pregnant liquor, scaling is inevitable. In multistage evaporator maximum temperature of the liquor reaches higher than 120–150°C, and the formed scale is typically washed by H₂SO₄. In the VRCE operation temperature, which can be selected arbitrarily, is very low and scaling rate is very low at our selected 80°C. Scaling rate (desilication rate) is estimated from the desilication rate equation (Oku, 1971) comparing VRCE to multistage evaporator and shown in Table 2.

Table 2 Estimation of Scaling Rate Difference between VRCE and 5-stage Flash Evaporator

	VRCE	5-stage Flash
Temperature, °C	80	50–128
C-Na ₂ O ₃ , g/l	130–158	130–158
SiO ₂ , g/l	0.50–0.61	0.50–0.61
Desilication Ratio of VRCE to Flash, Av., -	1	15
Max., -	1	52

Scaling rate in VRCE is expected very low compared to multistage evaporator from the calculation result.

Scaling is inevitable and we decided to wash it chemically by acid with corrosion inhibitor. Dissolution rate of scale was measured in a laboratory by HCl and H₂SO₄. HCl showed higher dissolution rate to some extent, then we applied the same HCL with the digestion section.

■ Sodium phosphate scale

Solubility of sodium phosphates is shown in Figure 6. Sodium phosphate in the spent liquor exists in equilibrium at evaporator inlet (shown as 50°C in the figure). It precipitates during concentration in case of multistage evaporator. But it would not precipitate in VRCE because solubility increases by preheating the spent liquor to 80°C at evaporator inlet and the temperature is kept constant inside the evaporator.

■ Sodium fluoride scale

Solubility of sodium fluoride is shown in Figure 7. Solubility of sodium fluoride shows very weak temperature dependency and it precipitates by concentration of the liquor.

The precipitated scale is water soluble and easily washes out by water.

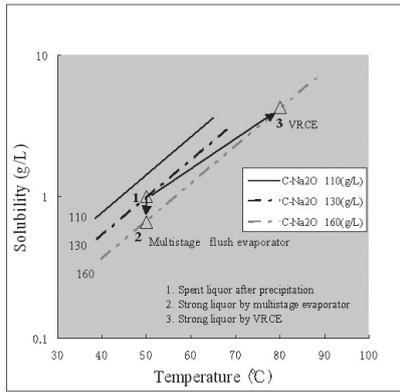


Figure 6 Solubility of Na_3PO_4 -family

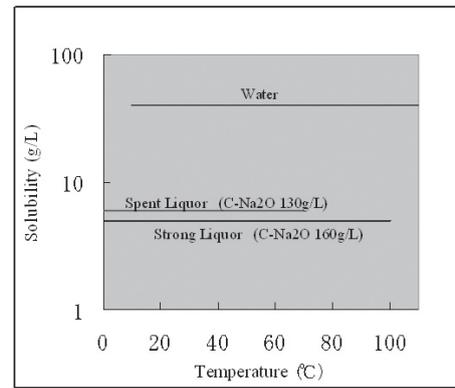


Figure 7 Solubility of NaF

3.3 Operation results of VRCE on the plant

3.3.1 VRCE and operation conditions

Sumitomo started plant operation in 1992. The plant was built by Sumitomo Heavy Industries. Main equipments of the VRCE and operation conditions are

- Evaporation
 - Design capacity, t/hr 60
 - Spent liquor feed, m³/hr 420
- Evaporator
 - Diameter, mm 6,800
 - Height, mm 10,000
 - Surface area (4 sections, each), m² 1,410
 - Material of heater SUS 304
- Liquor recycle pump (4 units, each), m³/hr 930
- Blower (parallel 2 units, each), Kw 1,350
 - Ps, kg/cm² abs 0.3347
 - Pd, kg/cm² abs 0.5957
- Spent liquor
 - C-Na₂O, g/l 130
 - Al₂O₃, g/l 67
 - Inlet temperature, °C 80
- Strong liquor
 - C-Na₂O, g/l 162
- BPR, °C 6.4–8.8 (Av. 7.6)

3.3.2 Change of heat transfer coefficient and effect of washing

Figure 8 shows the heat transfer coefficient change before washing and after washing on the plant after establishing the operation and maintenance conditions. Chemical cleaning by HCl for sodalite with corrosion inhibitor was performed every six month and water washing for sodium fluoride was performed every month. It is clear that the heat transfer coefficient is recovered to 4000–5000 J/sec·m²·K every after six months operation.

3.3.3 Energy consumption of VRCE

Table 3 shows the energy consumption of VRCE and five-stage flash evaporator which Sumitomo operated in the past. The five-stage flash evaporator was a design capacity of 25 t/hr-evaporation and operated by 17.5 t/hr.

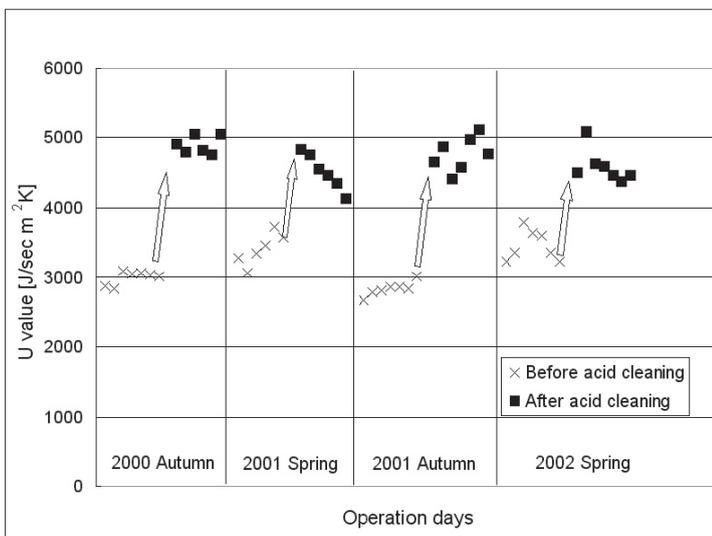


Figure 8 Heat Transfer Coefficient Change after 6 months operation and after acid cleaning

Table 3 Energy consumption of VRCE and 5-stage Flash Evaporator

	VRCE	5-stage flash evaporator*	
Evaporation rate, t/h	60.6	17.2	60.6
Steam, t/h	0.103	5.00	17.6
Electric power, Kwh/h	2,218	172	605
Evaporation ratio, -	-	3.44	
Steam, t/t-evaporation	0.002	0.29	
Electric power, Kwh/t-evaporation	36.6	10.0	
Steam, MJ/t-evaporation	5	816	
Electric power, MJ/t-evaporation	132	36	
Total energy, MJ/t-evaporation	137	852	

* Final stage vapor was discharged into cooling sea water through ejector

** Enthalpy of vapor was assumed to be 2.8 MJ/kg-steam

Energy consumption of VRCE is very low of about one fifth to sixth compared to five-stage evaporator.

Since the start-up of this plant, chemical cleaning has been repeated and the equipment material has been sound. And enormous energy saving is achieved by maintaining the high heat transfer coefficient by the chemical cleaning.

4 Future items

In the digestion process, Ca-contained scale is chemically cleaned by HCl keeping the equipment material sound by the addition of corrosion inhibitor. But too big scale even sodalite deposited for example in a pressure decanter was difficult to remove it chemically, it required hard work of manual elimination. It is required to establish a new way of cleaning or depressing scaling.

Sumitomo focuses products on chemical grades and the concentration of plant liquor is diluted compared to the latest SGA plant, then the liquor productivity is low. When VRCE is applied to latest SGA plant, BPR increases by increasing soda concentration. It will require higher efficient blower or compressor for re-compression of vapor, and then initial cost will increase. Optimum conditions should be decided from the overall economy including initial cost, operating cost and maintenance cost. It requires further study of impurity behavior in the concentrated liquor.

5 Conclusion

Ca-contained sodalite scale was easily cleaned by HCl. Plant equipment has been sound after a hundreds of cleaning by adding corrosion inhibitor. The inhibitor did not hinder the cleaning rate.

Falling film vapor re-compressive evaporator was applied to the plant, and operating conditions was established. The VRCE proved very low energy consumption (137 MJ/t-evaporation) by periodical cleaning of sodalite and sodium fluoride scale. The material is also sound by the addition of corrosion inhibitor.

References

- Ainscow, S. (2002) 'Falling Film Technology for Liquor Concentration, Experiences from a Recent Start-up', Proceedings of the 6th International Alumina Quality Workshop, Brisbane, Australia, pp 249–252.
- Duncan, A. (1996) 'An Investigation of Heat Transfer and Aluminosilicate Scaling in Bauxite Refineries', Dr. Thesis, University of Auckland, New Zealand
- Fortin, S., Breault, R. (2003) 'Bayer Process Heat exchangers Cleaning Efficiency: Optimizing the Acid Dissolution of Sodalite Scale', 2003 ECI Conference on the Heat Exchanger Fouling and Cleaning: Fundamentals and Applications, vol.RP1, Article 10, pp 68–74.
- Harato, T., Ishida, T., Ishibashi, T., Inami, M., Kumagae, Y., Murakami, M. (1996) 'The Development of a New Bayer Process that Reduces the Desilication Loss of Soda by 50% Compared to the conventional Process', 4th International Alumina Quality Workshop, Darwin, Australia, pp 311–320.
- Ishida, T., Takahashi, K., Sasaki, S. Applied (1993) 'Evaporation of Bayer Liquor', JP3440483B
- Mensah, J.A., Gerson, A.R., Jones, R., Zbik, M., 'Reduction of Sodium Aluminosilicate Scale in Bayer Plant Heat Exchangers', Light Metal (2001) pp 13–18
- Oku, T., Yamada, K. (1971) 'Dissolution of Quartz and the Rate of Desilication in the Bayer Liquor', Light Metal 1971, NY, pp 31–45
- Roach, G. I. D., Cornell, J.B. (1985) 'Scaling in Bayer Plants', CHEMECA, vol.85, pp 217–222.
- Yamada, K., Yoshihara, M., Tasaka, S. (1985) 'Properties of Scale in Bayer Process', Light Metals, p 223.