

A STUDY ON SCALE REMOVAL CHEMICAL FOR ALUMINA REFINERY

N.K. Kshatriya, S. Dasgupta, and P.K.N. Raghavan
Bharat Aluminium Co. Ltd., BALCO Nagar, Korba

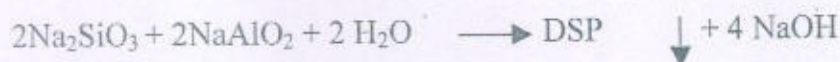
Abstract

During Alumina production by the Bayer Process, the Boehmitic bauxite ores are dissolved with caustic soda at elevated temperatures to extract the alumina hydrate. Most of the liquor silica content recrystallizes out as part of the red mud while the remainder is retained in the supersaturated sodium-aluminate solution used for hydrate precipitation. Subsequent to hydrate precipitation, the spent liquor is recycled via a series of heat exchangers for reheating and use in further bauxite digestion. Consequently, spent liquor heating in heat exchangers readily promotes scaling. Sodiumaluminosilicate scale formation in heat exchangers leads to serious tube-side fouling with a significant reduction in heat transfer efficiency and liquor throughput, resulting in increased energy and caustic soda consumption, higher labour demand, costly cleaning programme and loss of productivity. Acids cleaning, which is time consuming and causes acid corrosion generally remove the scales formed in the metal surface of alumina refinery.

This paper describes the dissolution of scales formed at different stages in an Alumina Refinery with combination of acid, descalent chemicals and Acid Inhibitor.

Introduction

Silica minerals are present in all bauxite ores, but the amounts vary largely among ores. Silica that is present as silicates, primarily clay minerals, dissolves quickly under typical Bayer digestion conditions. A majority of the silica subsequently precipitates as a Sodium Aluminosilicate (Sodalite or Desilicated Product – DSP) on the inside of the heat exchangers, pipelines and reactors according to the following reaction:



The actual silica concentration in Bayer liquor is always greater than equilibrium solubility and silica supersaturation is greater after the alumina precipitation step. Even though silica supersaturation increases during the gibbsite precipitation, very little silica precipitates with the alumina because of the low temperatures involved. As the alumina depleted liquor is reheated, either for evaporation or digestion of fresh bauxite, the rate of silica precipitation in the form of Sodalite increases markedly with the increasing temperature. The rate of DSP precipitation increases

exponentially with temperature; therefore, the highest precipitation rates are experienced on the transfer surfaces of the live steam heat exchanger. Scaling within the Bayer process is a wide problem both in terms of cost of removal and the human risk associated with descaling operations. The Sodalite precipitation as scaling on the inside of the heat exchange tubes is generally a cause for heat transfer loss and requires frequent shut down for cleaning and scale removal. A portion of the silica that precipitates as sodalite in the heat exchangers may be less than 1% of the silica in the liquor, but because of the large volumes of liquor involved, the Sodalite scale may be removed at a rapidly fast rate. The gibbsite scale that is formed is the end product of the process and constitutes loss of product.

There are several ways of protecting the heating surfaces and removing scale including magnetic and electric fluids, ultrasound, thermal treatment, mechanical cleaning, hydro-mechanical and chemical cleaning, used to soften and loosen scale.

The scales deposited on the metal tubes / pipes in an Alumina Refinery which produce Bauxite at high temperature and high pressure can be removed by the following methods:

Hydro-monitoring:

Removal of scales by high-pressure water jet has proved its efficiency and has recently found application in the industry. The scales on low pressure and high-pressure heaters are removed by this technique.

This method has a few shortcomings. In the course of cleaning, a large amount of contaminated water is formed that should be disposed. For feeding of cleaning head of Hydro-monitor into the tubes, all flange joints need to be dismantled.

Mechanical cleaning:

Cleaning of heating surfaces by manual poking using hammers is quite effective, but laborious and causes premature wearing and damage of the walls of the tube heaters. The scales of Digesters are removed by this technique.

Alkaline cleaning:

Plate Heat Exchanger (PHE) scales are removed by circulating raw caustic liquor (caustic soda solution, 400 g/l). This technique provides substantial loosening of scales since it was able to dissolve hydroaluminosilicates from the scales and binds Silica in hydrogarnets, but it is not effective in respect of Fe, Ti and P containing scales.

Acid Cleaning:

The problem of acid cleaning is the necessity of combining of the two alternative processes to dissolve all kinds of scales that are formed within all temperature ranges and at the same time to avoid acid corrosion of the tube. The scales of the evaporator units are removed by this technique.

The dissolution of scales depends on many factors:

- Acid concentration,
- Scale texture and structure,

- Thickness of scales,
- Reaction time,
- Conditions of formation and degree of crystallinity of scales,

Corrosion Inhibitor

An acid corrosion inhibitor protects steel surface during pickling / acid cleaning operation during hydrochloric acid. Inhibitor contains catalytic agent, which accelerates the conversion of nascent hydrogen into molecular hydrogen. This property suppresses adsorption of nascent hydrogen into the metal and curtails hydrogen embitterment. Thus Inhibitor provides a high degree of protection against corrosion and finds extensive application in inhibiting acid used for removing scales, rust and other impurities from the metal surface.

Laboratory Work

Descalcent chemicals and acid corrosion inhibitor from M/s. Deioners Specialty Chemical (P) Ltd., Delhi, was tested on the scale samples of Alumina Plant. The scale samples from low-pressure heater (LP), high-pressure heater (HP), Plate Heat Exchanger (PHE), Digester, Evaporators of Alumina Plant were collected separately. The method of the study was the following:

Solubility tests were carried out at ambient and at 65°C temperature with and without agitation and retained for periods till complete dissolution / removal is achieved.

Appropriate scale – to- Acid Ratio (SAR) was maintained.

After completion of the experiment scales were washed several times with water, dried up and weighed.

The studies of scales dissolution were carried out at various acid strengths and the descalcent concentrations to determine the most effective one for the scale dissolution. Technically, the acid strength would be proportional to the amount of deposit in the unit to be cleaned. Since the determination of the amount of deposit cannot be much more than a rough approximation and the general average conditions observed falls within a fairly narrow range, the strength of the solvent usually is set satisfactorily by laboratory experiment.

The dissolution of Digester scale was carried out for a constant dosage of descalcent and varying the concentration of hydrochloric acid. The results are tabulated in Table – I & Fig.1.

The solubility of digester scale was carried out for a particular acid concentration and varying the descalcent concentration. The results are given in Table – II and Fig. 2.

The dissolution of five scales samples from different units of Alumina Plant were tested in ambient and at 65 °C temperature. The results are given in Table – III.

In order to improve the solubility of the evaporator scale, the treatment of scale was conducted with intermittent stirring with glass rod and also with mechanical stirring. The results are shown in Table – IV.

Performance of Inhibitor

The purpose of Inhibitor in acid cleaning is to protect the base metal from corrosion and should not prevent the scale dissolution. The efficiency of the Inhibitor can be estimated by the Inhibition effect or the degree of protection. Inhibition effect indicates multiplicity of corrosion slowdown by the Inhibitor. Degree of protection characterizes completeness of corrosion.

For investigation of the efficiency of the Inhibitors, the annular portion of the tube used in the Digester and LP / HP Heater were filled with hydrochloric acid without and with Inhibitor (1:3 (W/V) of acid solution). The mixtures were kept at ambient temperature and held for sufficient time at 10 SAR.

The samples were taken out washed and weighed to determine the Inhibition effect and degree of protection. The performance of Inhibitor is given in Table - V.

TABLE - I
Solubility of Digester Scale in different Acid Concentration.

Strength of Descalent - 5% (W/V),
Temperature - Ambient
Time - Sufficient for scale dissolution..

S.N.	Strength of HCl (V/V) (Acid : Water)	% Solubility With Descalent	% Solubility without descalent
1	1 : 4.1	29.02	2.86
2	1 : 3.1	31.24	3.15
3	1 : 2.4	31.79	4.03
4	1 : 2.0	33.08	4.69

TABLE - II

Solubility of Digester Scale with variation in Descalent Concentration.

Acid Strength - 1:2 (v/v)
Temperature - Ambient
Time - Sufficient for scale dissolution.

S.N.	Concentration of Descalent % (W/V).	% Solubility
1	2.0	28.04
2	4.0	35.90
3	6.0	36.51
4	8.0	38.56

TABLE – III**Solubility of Scales at different Temperature.***Retention Time - 18 hours.*

S.N.	Source of Scale	% Solubility of Scale			
		Temp. – Ambient		Temperature – Ambient+ 28°C	
		* B	** SM	^x B	^{xx} SM
1	Low Pressure Heater (LP).	7.66	11.84	14.87	23.19
2	High Pressure Heater (HP).	10.80	19.08	11.99	31.62
3	Digester	9.51	30.15	23.97	48.89
4	Plate Heat Exchanger (PHE)	25.27	85.50	31.94	94.23
5	Evaporator.	100	44.73	100	58.79

* B (Blank) - 1 : 2 (V/V) HCl,

** SM - Mixture of 1 : 2 (v/v) HCl, 5% Descalent (w/v) & (Solvent Mixture) 1.3 % (v/v) Corrosion Inhibitor.

TABLE – IV**Solubility of Evaporator Scale.**

S.N.	Test Conditions	Dissolution Media	% Solubility
1	Intermittent Stirring with Glass Rod.	* B	100
	Temp. - Ambient Time - Sufficient for Dissolution.	** SM	84.48
2	Intermittent Stirring with Glass Rod.	* B	100
	Temp. - 70 °C Time - Sufficient for Dissolution.	** SM	91.63
3	Mechanical Stirring.	* B	100
	Temp. - Ambient (38°C) Time - Sufficient for Dissolution.	** SM	91.98

*B - 1: 2 HCl (v/v)

** SM - Mixture of 1:2 HCl (v/v), 5% Descalent (w/v) and 1:3% (v/v) Inhibitor.

TABLE - V

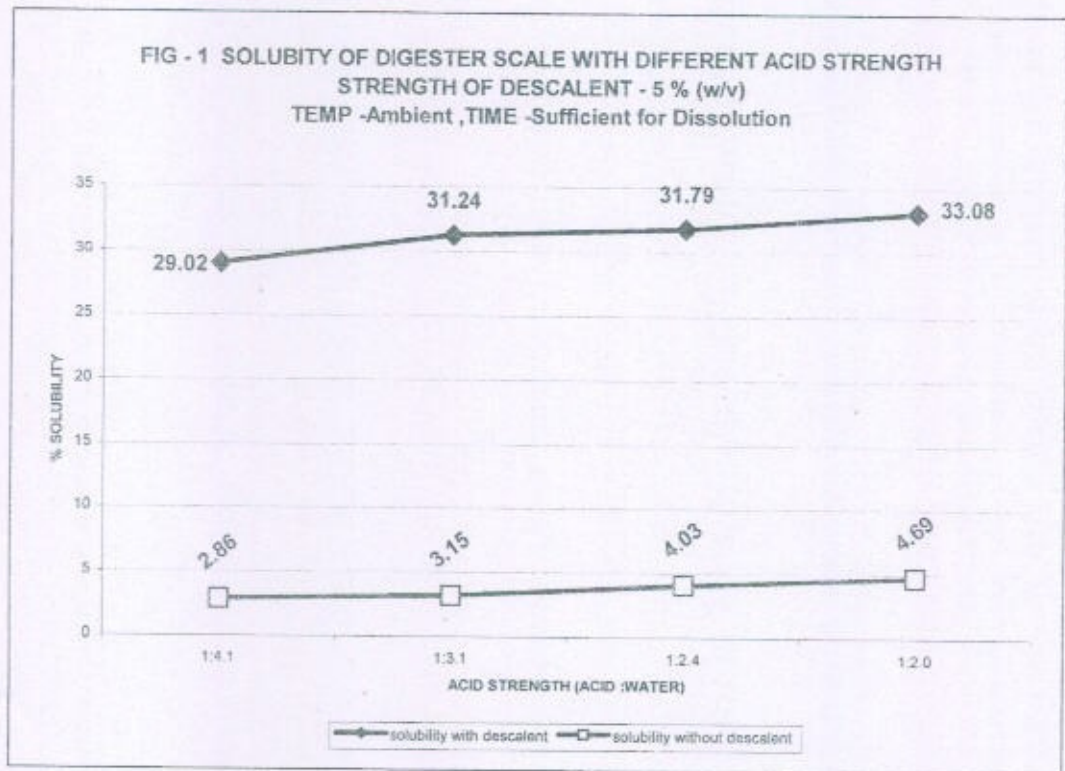
Preformance of Inhibitor.

Acid Strength (HCl) - 1 : 2 (v/v),
 Dosage of Inhibitor - 1.3% (w/v),
 Temperature - Ambient,
 Time - Sufficient for Dissolution.

S.N.	Sample Name		Corrosion Rate gm/m ² /hr.	*Inhibition Effect	**Degree of Protection %
1	Digester Tube	Without Inhibitor.	2.39	2.57	61.09
		With Inhibitor	0.928		
2	LP / HP Heater Tube	Without Inhibitor.	2.67	5.89	83.02
		With Inhibitor	0.453		

* Ratio of corrosion rate without Inhibitor and with Inhibitor.

** $100 - [1 - (1/\text{Inhibition effect})]$



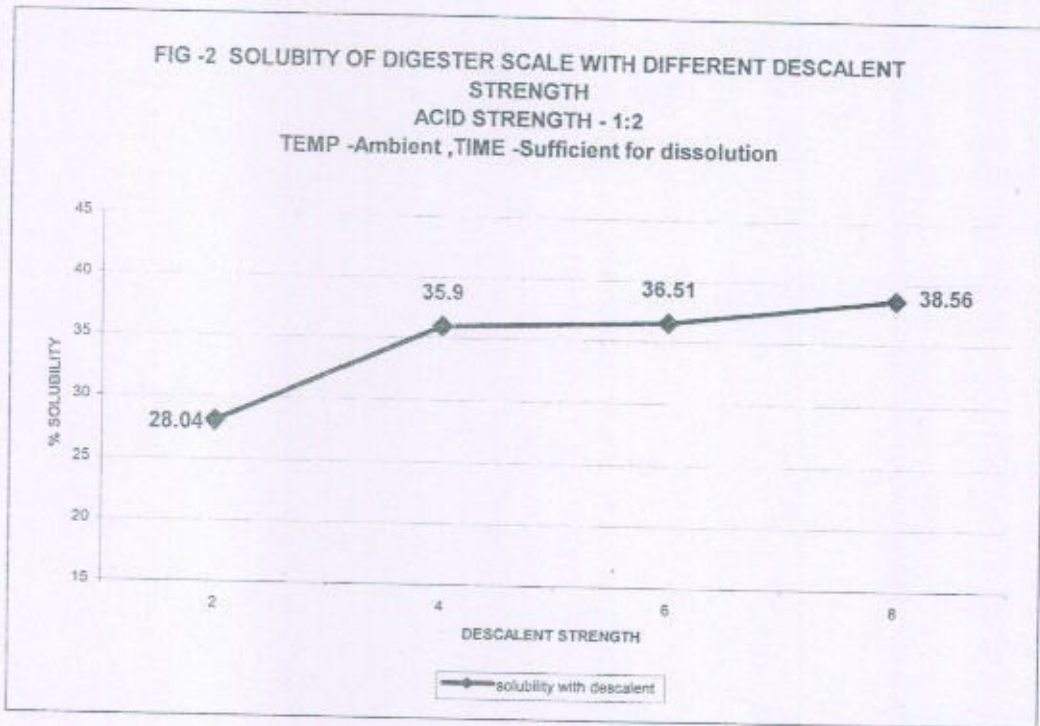
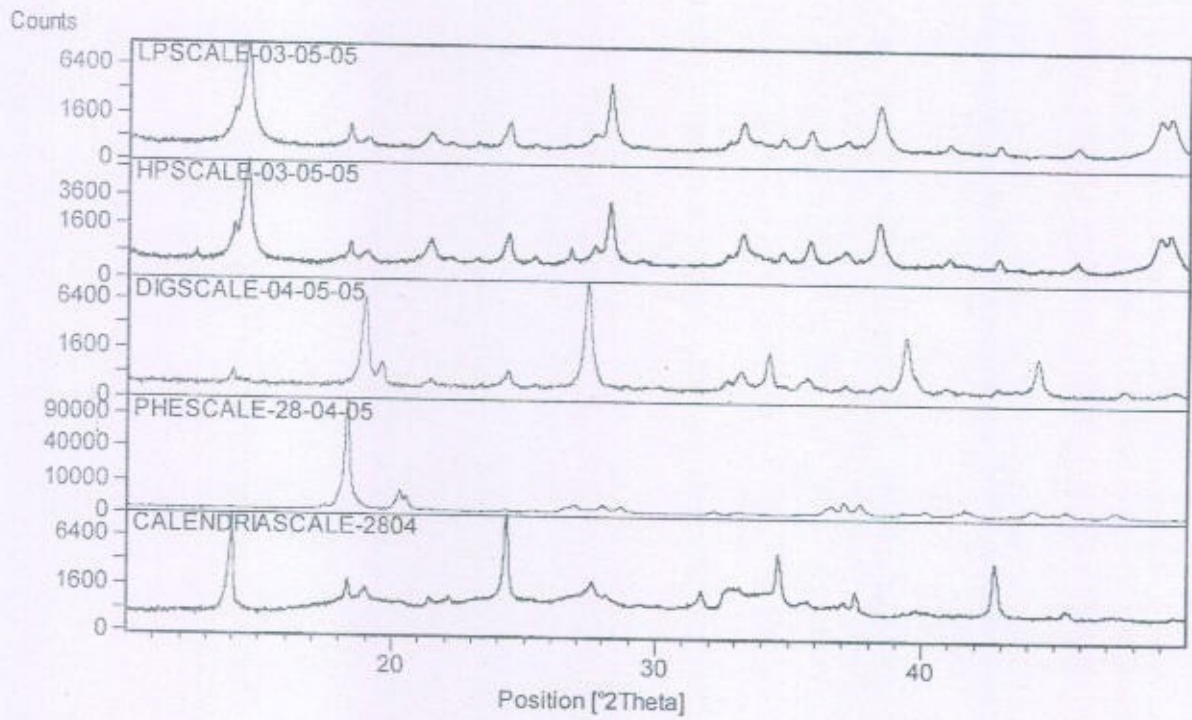


Fig - 3 , X Ray Diffraction of Scales



X-ray Diffraction of Scales

In the course of bauxite digestion in the Bayer cycle together with dissolution of alumina containing components, dilution of accompanying minerals takes place that results in formation of new phases in red mud and their deposition as incrustation scales on heating surfaces. The majority of phases occurring in scales are not encountered in bauxite. A scan of different scale samples were presented in Fig -3. The major phases found by XRD in different scales are given below -

SN	Location of Scales	Temp, °C	Major Phases
1	LP Heater	95-100	Bohemite, Gibbsite, Sodalite
2	HP Heater	135-140	Bohemite, Gibbsite, Goethite, Sodalites, Hematite
3	Evaporator	60-65	Cancrinite, Sodalite Calcium - Titanate, Ilmenite Hematite
4	Digester	240	Cancrinite, Sodalites Calcium - Titanate
5	Plate Heat Exchanger (PHE)	85	Gibbsite

Discussion

From the experiment conducted, the following conclusions can be drawn:

- (1) It can be seen from the Table -I and Fig -1 that the solubility of scales increased with increasing the acid concentration.
- (2) The solubility of scales increased with increasing the strength of descalent. (Table-II and 2)
- (3) The solubility of scales increased with solvent mixture (Descalant and HCl) compared to treatment with HCl alone. It can be also seen that the solubility of scale increased with increasing the temperature of dissolving media (Table-III)
- (4) From the Table- IV, it can be seen that the stirring mechanism improves the solubility of evaporator scale.
- (5) It was observed that the corrosion rate decreased on use of Inhibitor (Table-V).
- (6) It was found that the solubility of scales shows differences in the solubility behavior depending on its constituents.
- (7) The low solubility of Evaporator and Digester scales are due to presence of major phases Cancrinite, Sodalite. The high solubility of PHE scale is due to presence of Gibbsite. The low solubility of LP and HP scales may be due to major peaks Boehmite.

Conclusion

From the laboratory experiment it can be seen that a dosage of 5 % mixture of descalent with 1.3 % of Inhibitor and 1:2 HCl gives considerable effect at 65⁰C temperature .The advantage of the descalent mixture achieved in preventing metal loss and corrosion from the tubes /pipes.

Acknowledgement

The authors are thankful to the management of Bharat Aluminium Co. Ltd., Korba for granting permission for presenting the paper. The authors would like to thank Mr. T.L. Palani Kumar Managing Director, Aluminium Business, and Mr. C.P.Baid, Director, Balco-Korba for their encouragement during the course of this work.

References

1. Donald Spitzer and others, Reagents for the elimination of sodalite scaling, Light Metals (2005) pp-183-188
2. A.G.Suss and others, Tube Digesters Protection of heating surfaces and scale Removal Light Metals (2004) pp137-142.