CHARACTERISTICS OF INCRUSTATIONS FORMED IN HIGH TEMPERATURE TUBE DIGESTORS

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Abstract

In 2006 – 2007, pilot and industrial trials were conducted on a high-temperature digestion unit utilising shell and tube heaters. Scales formed on the heating surfaces during refinery testing were extensively characterised and the resultant data correlated with heater performance over the commissioning period.

The paper examines the elemental and phase distributions in the various scale samples as a function of temperature, covering the range from ~45 to 270°C, and establishes the impact of identified components on heat transfer properties. Deposition of hydroxylapatite, $Ca_5(PO_4)_3OH$, was favoured in a temperature range from 160 to 220°C and was found to have the most deleterious effect on heater efficiency.

Notation and units

Na_2O_t - titratable (total) alkali;

Na_2O_c - caustic alkali (NaOH and $NaAl(OH)_4$);

$\alpha_c = \frac{Na_2O_c \times 1,645}{Al_2O_3}$ - caustic ratio of liquor (molar ratio of Na_2O to Al_2O_3)

1. Introduction

For alumina refineries processing boehmitic – diasporic bauxites, one of the most effective ways for achieving efficiency improvements is to install (and maintain) slurry heaters. Heat transfer factors and Reynolds number of flow through the heater tubes should be at levels as high as practicable, i.e. peak efficiency of heat and mass exchange processes. This concept has been applied in the design and construction of a high-temperature digestion unit at the Uralsky Alumina Refinery in Russia that utilises shell and tube heat exchangers of a new design (termed TU HTD in the following text).

The key advantages of this new equipment and process flow sheet are a decrease in the specific steam consumption, for lower capital cost. However, during the operation of the high-temperature slurry heaters, scale deposition on the heating surfaces negatively impacted the thermodynamic characteristics of the heat exchangers, leading to productivity losses. This paper examines the kinetics of scale formation in the new shell and tube heaters during the commissioning period. Chemical and phase analysis of scale samples collected from the tube surfaces have been conducted and the distribution of chemical species (SiO_2, P_2O_5 etc) and phases in the incrustations established as a function of digestion temperature. Further to this, these data have been correlated with the heat transfer characteristics of the individual heaters. Finally, recommendations are made in methods and modes for cleaning these shell and tube heaters.

2. Brief description of digester operation and conducted trials

The trials were conducted using boehmite - chamosite bauxite from Sredny Timan, which is located in the north of the European part of Russia. The digestion process for this type of bauxite requires high-temperature slurry heating to achieve maximum recovery of aluminium oxide from the ore into the green liquor; the final digestion temperature used during the trials was 260-268°C. The selection of slurry velocity was based on several factors, these being (i) the need to provide an adequate heating / temperature profile; and (ii) minimisation of the rate of scale formation on heating surfaces, whilst not creating flow conditions conducive to pipe erosion It was experimentally determined via pilot trials that the optimal slurry velocity through the heating tubes should be ≥1.8 m/s; during the plant trials the slurry velocity was about 2 m/s.

For heating of crude slurry, 3-pass heaters with heating tubes of dimensions 32×2 mm were used. At the given slurry flow rate, the total slurry heating time to reach the reaction temperature (260-268 ºC) was about 2 minutes 34 seconds, with the slurry retention time in one tube of a heater of «П» type being about 3 seconds (refer to Figure 1 below).

The crude slurry heating profile in the TU HTD covers the range 45-268°C. Heating from 45-200°C is carried out by means of steam available at the factory (pressure: 2.8 MPa, temperature: 300°C). Higher temperature heating from 200-268°C is provided by steam at a pressure of 9.0 MPa and temperature 320°C supplied from a purpose-built boiler.

The TU HTD trials were conducted with the temperature profile presented in Table 1.

A block diagram of the TU HTD digester is shown in Figure 1.

Table 1. Temperature operating mode of digester

Heater	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Slurry temperature, °C	77	110	133	155	168	173	190	190	200	222	242	253	263	268

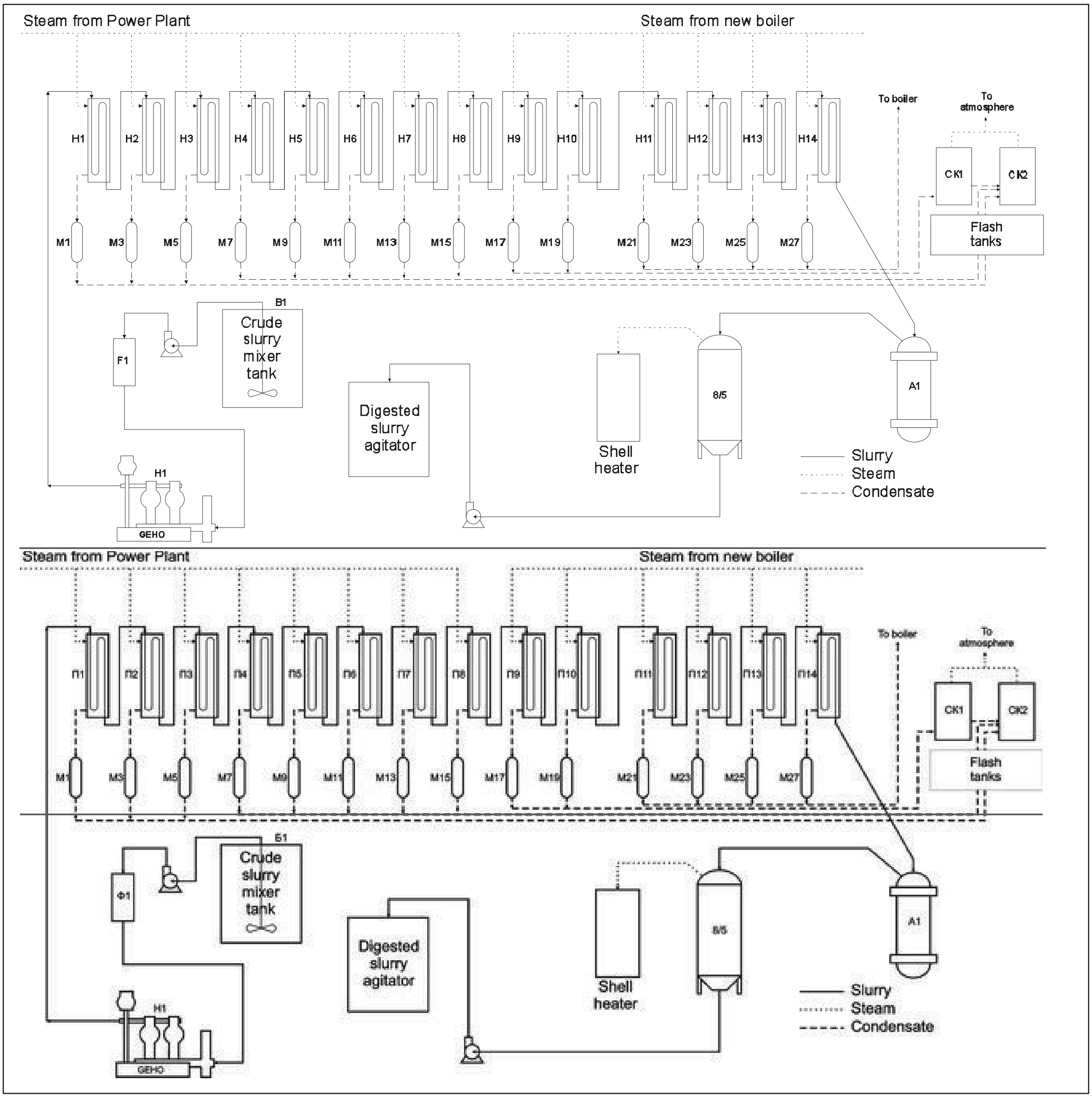


Figure 1. Process block diagram of TU HTD

Crude slurry is predesilicated at 95°C for 8 hours before being pumped into a mixer tank, where it is cooled to a temperature of 45°C. From the mixer tank the crude slurry is pumped through a filter, after which additional propulsion via a GEHO pump is used to send the crude slurry through the heaters H1- H14 to the autoclave A1 (residence time in A1 is ≥ 20 minutes).

Technological operating mode of the unit was as follows:

Crude slurry flow rate: 4.5 m^3/h.
Crude slurry input temperature: 45°C.
Crude slurry output temperature: 260-268°C.
Estimated caustic ratio of digested slurry: 1.38-1.43.
Slurry velocity: ≥1,8 m/s.
Slurry density: 1370 kg/m^3.
Retention time in autoclave A1 at least 20 minutes.

Typical analyses of the Sredny Timan bauxite and the crude slurry are presented in Tables 2 and 3.

Table 2. Bulk chemical analysis of the Sredny Timan bauxite mass %

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	V_2O_5	Cr_2O_3	MnO
7.0	49.4	28.0	3.1	0.22	0.29	0.44	0.15	0.16	0.07	0.06	0.45

Table 3. Crude slurry analysis

Na_2O_t (g/L)	Na_2O_c (g/L)	Al_2O_3 (g/L)	α_c
155 ± 10	139 ± 10	83 ± 3	2.75

3.0. Study of scales

The TU HTD plant trial was conducted for a period of 20 days, during which there was a decrease in the heat transfer factor by 50 % (average through the unit). At the end of the trial period, RUSAL VAMI personnel collected samples of scale from the heating surfaces of each of the TU HTD heaters. The observed scale thickness in each heater as a function of crude slurry temperature is shown in Figure 2.

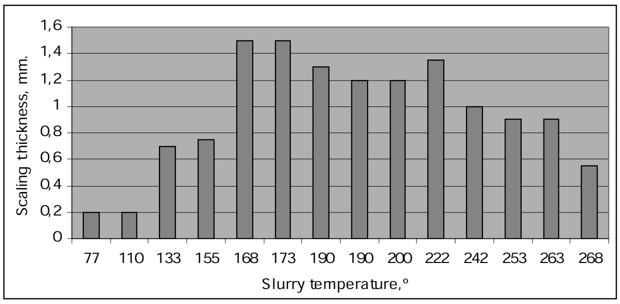


Figure 2. Scaling of the heating surface versus slurry temperature

Chemical and phase analyses of the scale samples were conducted in the RUSAL VAMI Laboratory and subsequent plotting of these data against slurry temperature revealed the relationships presented in Figs 3, 4 and 5.

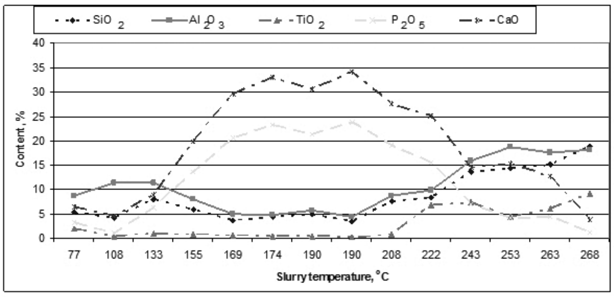


Figure 3. Elemental distributions in the scale samples versus slurry temperature

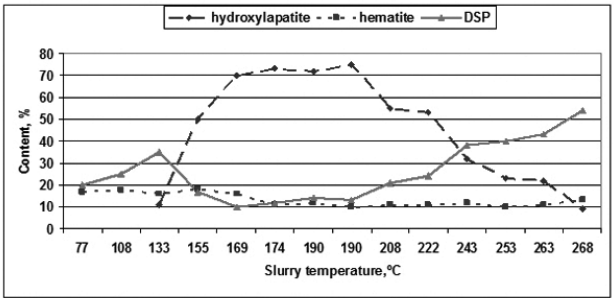
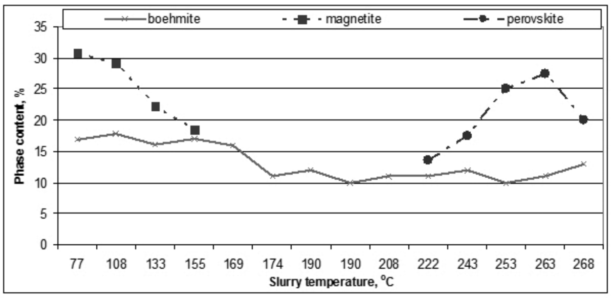
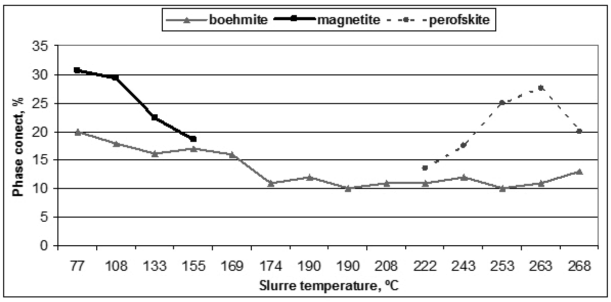


Figure 4. Distribution of hydroxylapatite, hematite and DSP in the scale samples versus slurry temperature

From Figs 3, 4 and 5, the influence of slurry temperature on the major phase and elemental distributions in the scales is visible:

- At the initial temperatures of slurry heating from 45-130 °C, the scales and deposits are mainly represented by iron components, primarily in the form of magnetite (Fe_3O_4);
- In the temperature range from 130-200 °C, iron is deposited to a lesser degree and the active crystallization of calcium and phosphorus dominates in the form of hydroxylapatite ($Ca_5(PO_4)_3OH$);
- At temperatures above 220 °C, there is a reduction in hydroxylapatite content and concomitant increase in aluminum and silicon deposition in the form of sodium hydroaluminosilicate ($Al_2O_3{\cdot}Na_2O{\cdot}nSiO_2{\cdot}H_2O$);
- In the temperature range 240-268 °C, there is significant co-deposition of calcium and titanium in the form of perovskite ($CaO.TiO_2$), with minor quantities of $MgHPO_4{\cdot}3H_2O$ also formed;





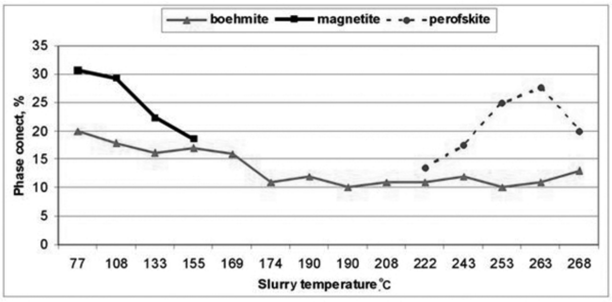


Figure 5. Distribution of magnetite, boehmite and perovskite in the scale samples versus slurry temperature

- Hematite (Fe_2O_3) is present in all the deposits (irrespective of the slurry temperature);
- Deposition of aluminum in the form of boehmite $Al_2O_3{\cdot}H_2O$ is observed only at temperatures 45-110 °C.

The decrease in the heat transfer ratio for each heater over the trial period is displayed in Figure 6 (shown as a percentage):

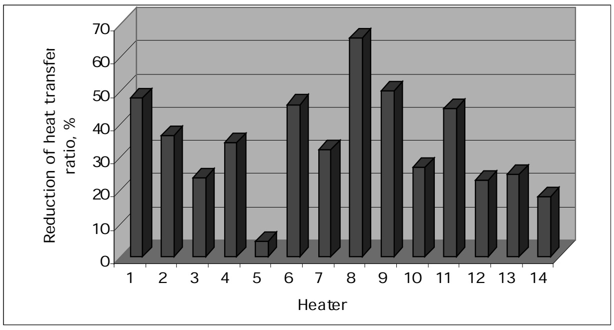


Figure 6. Reduction of heat transfer ratio through the heaters

Having defined the magnitude of the heat transfer ratio decrease over the duration of the trial, it is possible to determine values for heat conductivity for the scales.

The heat conductivity factor for each heater was defined through the established value from the ratio:

$$K = \frac{1}{(1/\alpha_s) + (\partial_{st}/\lambda_{st}) + (\partial_{sc}/\lambda_{sc}) + (1/\alpha_p)}$$

Where k – heat transfer factor, kcal / (m²·h·°C)

α_s - heat transfer factor from steam to the wall, kcal / (m²·h·°C);
α_p - heat transfer factor from the wall to slurry, kcal / (m²·h·°C);

∂_{st} - thickness of the wall, m;
∂_{sc} –thickness of scale, m;
λ_{sc} – heat conductivity of the deposit, kcal / (m^2·ºC);
λ_{st} - heat conductivity of steel, kcal / (m·ºC).

At the commencement of the trial, it can be assumed that the heat conductivity of all heater walls was identical and equal to the heat conductivity of the steel from which the heater tubes were made. The corresponding heat conductivity factor, λ_{st}, is 45 kcal / (m·ºC).

The heat transfer factor from the wall to slurry depends on the thermodynamic and physical properties of the slurry and remains invariable during the trial. The heat transfer factor from condensing steam to the wall depends on the slurry temperature and steam parameters (temperature and pressure) and is specific to each heater. Note that under operational conditions, steam parameters for each heater were regularly varied to maintain the required temperature mode. Taking this into account, the heat transfer ratio from the steam to the wall was calculated using the steam parameters corresponding to stable operation of the digester. Therefore, the factors obtained for heat conductivity may differ from the actual values. It is necessary to note that the heat conductivity factor is a composite function of numerous parameters and in most cases is defined experimentally.

The values obtained for the heat transfer coefficients for individual heater scales are shown in Figure 7:

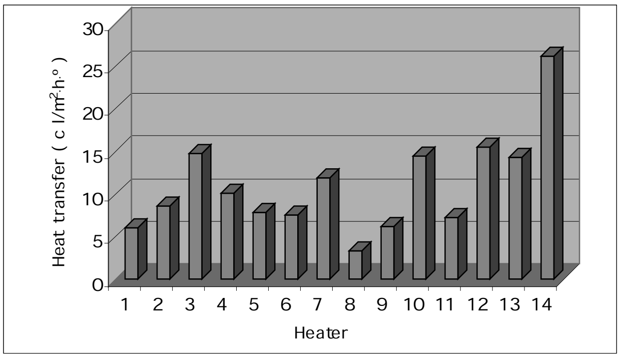


Figure 7. Heat transfer factors for heater scales

From Figs 6 and 7 it can be seen that the maximum decrease in both heat transfer and heat conductivity factors is observed mainly in the middle heaters (П6-П10) that is in a temperature range 160-220 º C. In the same area there is a considerable decrease in the heat transfer through the incrustations. The results of x-ray analysis and quantitative determination of phase components show that within this temperature range there are three main phases: hydroxylapatite $Ca_5(PO_4)_3OH$, hematite, Fe_2O_3, and DSP, $Al_2O_3{\cdot}Na_2O{\cdot}nSiO_2{\cdot}H_2O$. Hydroxylapatite is the dominant species and its concentration reaches a maximum in this temperature range. By comparison, the hematite content in the scales changes only slightly over the whole temperature range. DSP content fluctuates at levels of 15 - 20 %, with appreciable deposition noted in two temperature intervals: 100-130 ºC and 200-268ºC. It is hypothesized that the key influence on heat conductivity of the heaters in the temperature interval 160-220 ºC is connected with the hydroxylapatite content prevailing in the scales.

In the last heaters (at temperatures of 200-268 ºC), the DSP content reaches 40-50 % of the total mass of scale, whilst titanium deposition in the form of perovskite, $CaO{\cdot}TiO_2$, also occurs. It is interesting to note that despite scale thickness in these heaters being typically about 0.9 mm at the end of the trial, there was only minimal deterioration observed in the heat exchange properties of the last heaters. That is, DSP / perovskite scales still allow comparatively high heat transfer ratios. In the two upstream slurry heaters (temperature range 45 - 110 ºC), heat conductivity of the deposits is at a comparatively low level, but the scale thickness on the heater tubes did not exceed 0.2 mm. Various phases were present, with the major components being magnetite (Fe_3O_4), at a concentration about 30 %, DSP at a content in the order of 20 % and boehmite ~10 %. Significantly, a minor calcium component not in the form of hydroxylapatite, but as calcite ($CaCO_3$) was present in these scales. It is suspected that this is the reason for the considerable decrease in heat conductivity of those heaters, since the heat conductivity of calcite itself is very low, ~0.5 kcal / (м·ºC).

Figure 8 shows the variations in the content of the major phase elements (hydroxylapatite, hematite and DSP) in the deposits, together with the heat conductivity factor, as a function of slurry temperature:

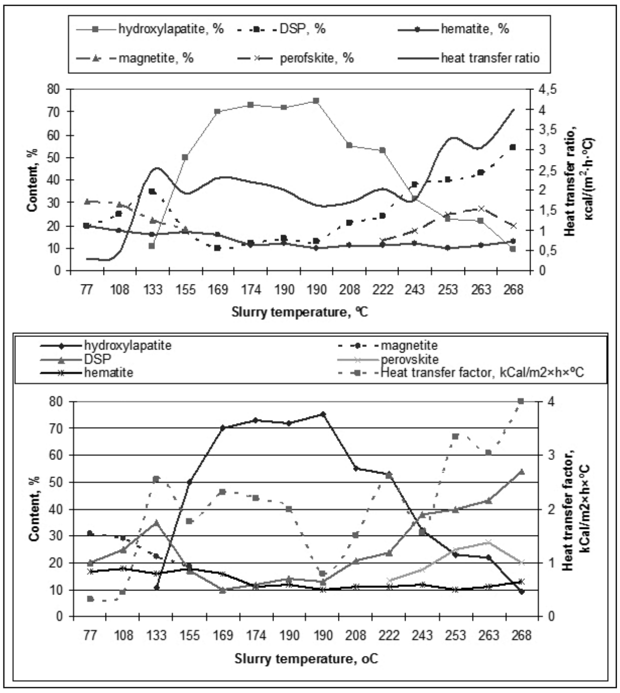


Figure 8. Phase distributions and heat transfer ratio of the deposits versus slurry heating temperature

Below is given the summary of heat transfer ratios obtained in the course of trials (Table 4).

Table 4. Heat transfer rates for the heaters

Heating temperature range °C	Heat transfer factor, kCal/m²×h×ºC		
	Initial value	Final value (20-25 days of operation before cleaning)	Average operational value
From 45-50 to 170-180	1500-1600	900-1000 **	1200 - 1300
From 170-180 to 268	1000-1100*	650-750 **	850 - 900

* Relatively low initial factor of heat transfer is connected with difficulties in cleaning the heating surface.

** The wide range is caused by variability in the scaling rate, and also by the different phase characteristics, density, heat conductivity, etc. Rate of scale formation varies from 10-20 to 100 microns/days.

4. Cleaning of heating surfaces

The findings from the investigations described above have been used to formulate a cleaning regime for the TU HTD unit at Uralsky and also in design considerations for the greenfield refinery at Sosnogorsk.

A cleaning cycle is implemented after a period of 20 days operation of the TU HTD unit and involves a two step process:

- Cleaning of all heating surfaces by application of a steam-condensate mix for at least 24 hours; followed by,
- Mechanical descaling of the heating surfaces of the shell and tube heaters operating in the temperature range 170-268 ºC by means of hydro-jets providing a stream pressure of at least 1300-1500 atm. Hydroblasting of the lower temperature shell and tube heaters (i.e. those operated in the range 75-170 ºC) is conducted only as required.

Note that chemical cleaning of the heat exchangers using an acid / inhibitor mix is not effective, as the calcium phosphate component of the scale is chemically resistant.

5. Conclusions

Based on the data obtained for phase composition, scale thickness and heat transfer factors from plant trials of a new type of shell and tube heaters designed for processing a high-silica, boehmitic bauxite, the following can be concluded:

- Scaling rate on heating surfaces is strongly dependant on slurry temperature. In our case, maximum deposition is observed in the temperature range 160-220 ºC.
- The primary influence on heat conductivity of deposits in the temperature interval 160-220 ºC is due to the presence of hydroxylapatite. At the maximum scale thickness (1,5 mm), heat conductivity decreased by ~ 2 times.
- High DSP and perovskite contents in scales formed in the final (high-temperature) stages of heating are associated with only minimal deterioration in heater performance. The thickness of scales deposited in this temperature range was typically 0.9-1.0 mm, yet a relatively high heat transfer ratio was maintained.
- Low heat transfer associated with scales taken from the initial heaters is considered to be due to the calcite and magnetite content in these deposits.
- Considerable variation in the heat transfer properties of the heaters are related to changes in scale thickness.

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