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STUDY OF FILTRATION AND WASHING OF RESIDUE AFTER HCL LEACHING OF KAOLIN CLAY

Alexander S. Senyuta, Andrey V. Panov, Alexander A. Damaskin, Andrey A. Smirnov

UC RUSAL Engineering and Technology Centre (VAMI), Saint Petersburg, 199106, Russian Federation

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Abstract

One of the process stages of kaolin clay processing to alumina is solid-liquid separation process after HCl leaching with subsequent washing of silica residue. Our laboratory studies have shown that of existing equipment most efficiently for this task pressure filter can be used. Slurry after hydrochloric leaching is amenable to filtration under 5 bar pressure with good parameters, in spite of material being fine (relatively d_{50} = 17 μm). Type of filter media has no significant influence.

The main process parameters were established in the lab scale using press filter with washing. It was also noted that after fourfold washing, filter capacity (by filtrate) was reduced from 2.5-3 to 0.3-0.6 $m^3/(m^2 \cdot h)$. Study of these phenomena by means of XRD and Electron Microscopy analysis showed that the reason is gelation of amorphous silica while pH of washing water approaches 7.

1. Introduction

Kaolin clays are the most appropriate natural raw materials for the production of alumina by hydrochloric acid method [1, 2]. The reasons for this are their prevalence, availability of deposits, huge reserves, relatively easy hydrochemical recovery of the target component, low content of compounds with soluble impurities (iron, calcium, magnesium, sodium, potassium).

One of the important process steps is separation of the digestion slurry into solid and liquid phases, after acid leaching of the raw material. The previous research experts indicated the challenges of the process due to using sulfuric acid as leaching agent [3].

The acid slurries by their physical-chemical and rheological properties are similar to red mud of the Bayer process. The availability of large amount of finely dispersed phase leads to low productive filtration process and requires sophisticated equipment, i.e. hyperbaric filters [4]. However, for aggressive acid media a special corrosion proof version of such equipment is required, making difficult the use of complicated equipment in this application. The most available is application of vacuum belt filters or press filters. Moreover, emissions of acidic vapors and aerosols using press filters are much lower.

In our previous publication [2] a brief efficiency estimate of slurries filtration after hydrochloric acid leaching of kaolin was provided.

This study provides a more complete view of this process and allows comparing the parameters of different filtration methods and washing of silica residue.

2. Slurry preparation

For preparation of fresh slurry to filtration a preliminary leaching of kaolin clay from one of Russian deposits was carried out containing, %: SiO_2 56.8; Al_2O_3 27.1; Fe_2O_3 2.0; $TiO_2$0.48; CaO 0.45; Na_2O 0.31; K_2O <0.15; MgO 0.27; P_2O_5 0.05; LOI 11.8.. The X-ray analysis of the ore sample demonstrated kaolinite content 69.3 %, alpha-quartz - 24.7 %. Particle size distribution of the initial kaolin clay is presented in Table 1.

Table 1. Particle size distribution of initial kaolin clay

Particle size, μm	Mass fraction, %	Particle size, μm	Mass fraction, %
<1	9,99	<63	94,58
<5	38,94	<75	95,74
<10	54,96	<100	97,50
<20	72,36	<125	98,99
<45	89,31	<150	99,75

Leaching was conducted during 3 hours using 20% hydrochloric acid and temperature 170°C in a multi autoclave unit with microwave heating and magnetic stirring with HCl stoichiometric excess to the sum of soluble oxides 10%. The unit allowed producing 600 ml of slurry after one experiment.

3. Vacuum filtration

After the leaching the content of all autoclaves were cooled down to 50-60°C, discharged into Buchner funnel equipped with paper filter on a drainage polypropylene cloth. The effective cross-section of laboratory filter was 0,013 m^2. During filtration the under pressure was maintained at the level 0.6 Bar. After visual disappearance of liquid phase on the surface of solid phase the filtrate was removed, the silica residue was covered with one more paper filter to avoid dilution and 250 ml of hot water was added to displace the Al chloride liquor. The time of filtration and washing was recorded. The wash water was discharged again and the silica residue was washed once more by 1- 1.5 l of hot water. The silica residue was dried and analyzed.

Average production rate of filtration under above conditions with thickness of washed layer 16 mm was 102.5 $kg/(m^2 \cdot h)$ of dry silica residue and 0.33 $m^3/(m^2 \cdot h)$ of filtrate. The silica residue moisture on the filter was 55.1 %. It is considerably below the parameters achieved by USBM research experts on the belt filter [5], and should be explained by the specifics of the used ore material. It should be noticed that at filtration of slurry, mineral composition of ore is also crucial for sulfuric and nitric acid solutions [3].

4. Pressure filtration

In a designed laboratory filter the principle of "liquid" piston, pushed by compressed air was used modelling operation of press filter. The filtering unit with diameter of filter partition 16.7 mm and temperature control of separated media is presented in Fig. 1. The details of the unit are fabricated of high density polypropylene and polyethylene.

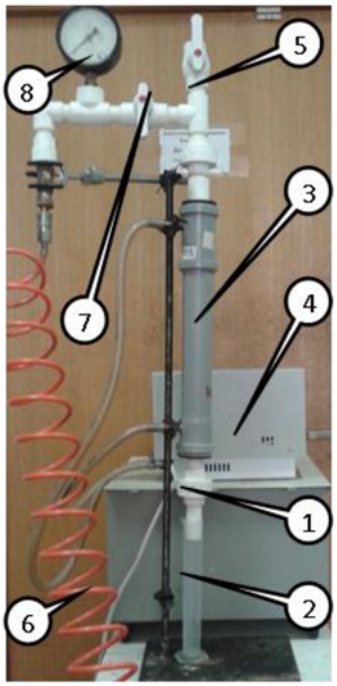

Figure 1. Laboratory unit for filtration of acid slurries under pressure

1- filtering partition; 2- filtrate collector; 3-heating water jacket; 4- water bath; 5 – slurry feed valve; 6 – hose of compressed air from compressor; 7 – compressed air valve; 8 – pressure gauge.

The experiment was carried out as follows.

Before the experiment, in the slot 1 (Figure 1) the filtering partition 1 fabricated of polypropylene filter cloth was set and sealed with a captive nut. The water bath 4 with external circulation loop via jacket 3 for unit heating was switched on and the required process temperature was fixed. Compressor with air receiver equipped with supply hose 6 was switched on and a pressure 5 bar was set. Further via the open valve 5 and closed valve 7 the slurry through funnel was added. The valve 5 was closed and valve 7 was opened and by compressed air the slurry was pressed through filtering partition. The filtrate was collected in the graduated cylinder 2. The filtration process was considered completed after the air leakage via the silica residue layer on the filter accompanied by specific sizzle. The time of filtration was recorded for further calculation of production rate.

The experiments were carried out by varying the thickness of filtering layer and slurry temperature. The obtained results are presented in Table 2 testifying that pressure filtration provides higher production rate of the process as compared to vacuum filtration.

Table 2. Pressure filtration parameters

	Filtration performance			
	by filtrate, $m^3/(m^2 \cdot h)$		by dry residue, $kg/(m^2 \cdot h)$	
Temperature, °C / Layer thickness, mm	20	90	20	90
4	1654	266	827	1329
8	624	68	312	340
12	604	65	302	325
16	384	-	192	-

For determination of filtering property of the stable washed silica residue layer on the filter during the following set of experiments the filtrate from the previous test was added on filter to prolong the infiltration process. In appeared that in each specific case the infiltration rate was not changed during 90 minutes that testifies the stable permeability of the silica residue.

5. Washing of silica residue on the pressure filter

For the experiment of silica residue washing under pressure a unit presented in Figure 2 was implemented including the supporting plate 1 with a hole in the center for drainage pad 2 and opening for filtrate discharge and elastic ring packing 3. When assembled a cylindrical operating chamber 4 is supported on the edge by ring packing 3 and fixed by clamping screw 5. The filling of slurry in operating chamber is provided over a ball valve 6 using the funnel. The supply of compressed air is provided by a hose 7.

The metal parts of the unit are made of stainless steel, the drainage pad – solid polyvinylchloride, elastic packing – vacuum rubber. The unit also simulates the operation of press filter and realizes the "liquid" piston principle, pushed by compressed air.

The diameter of filtering partition is 97 mm with open area 72 cm^2 which exceeds by more than 30 times the corresponding parameter of the filtration unit described above. The volume of operating chamber is 0.95 liter, providing maximum batch dosing of slurry 0.7 liter.

The filtration procedure was as follows.

On the supporting plate a piece of filter cloth or paper was placed, the operating chamber was sealed by hold-down screw. Further through the open ball valve the slurry or wash water was added. The valve was closed and the compressed air was supplied. By the pressure of compressed air the slurry was pressed over the filtering partition. The filtrate was collected in the vessel below the supporting plate. The filtration was completed after the air leakage via the silica residue layer on the filter accompanied by specific sizzle. The time of filtration was recorded for further calculation of production rate.

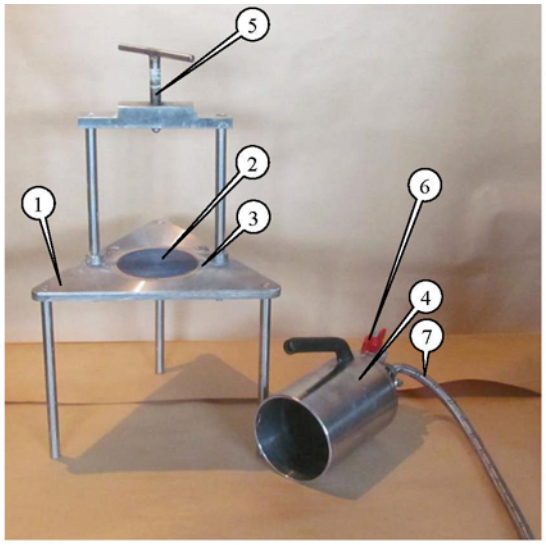

Figure 2. Large scale lab filter unit

1 – supporting plate; 2 – drainage pad; 3 – elastic ring packing; 4 – operating chamber; 5 – hold-down screw; 6 – feeding valve; 7 – air hose.

For slurry preparation 164 g of silica residue with humidity 61% was reslurried in 200 g of cold water (20°C) the resulting slurry was filtrated. Further, not disassembling the filter, the formed layer of silica residue was washed in the infiltration mode by water (400 ml). Then the filter was disassembled, the silica residue was removed and the procedure was repeated.

The washed silica residue analysis, %: Al_2O_3 2.38; SiO_2 90.50; CaO 0.11; TiO_2 0.70; Fe_2O_3 0.15; MnO <0.01; MgO <0.1; Na_2O 0.15; K_2O 0.09; LOI 3.22.

XRD of silica residue: alpha-quartz, microcline, mica, XR amorphous phase.

Particle size distribution is presented in Table 3.

Table 3. Particle size distribution of silica residue

Particle size, μm	Mass fraction, %	Particle size, μm	Mass fraction, %
<1	4,44	<63	92,22
<5	22,88	<75	99,75
<10	36,44	<100	99,91
<20	54,93	<125	100,00
<45	81,51	<150	100,00

Data of Tables 1 and 3 show the increase in average size of particles of leached material as compared to raw material. This can be explained by increasing of alpha-quartz content because alpha-quartz is not leached by HCl. During the leaching reactive material is dissolving in the acid, that leads to reducing the size of reactive particles and increasing the average size.

Silica residue presents finely dispersed material with part of particles with low crystallization (Figure 3).

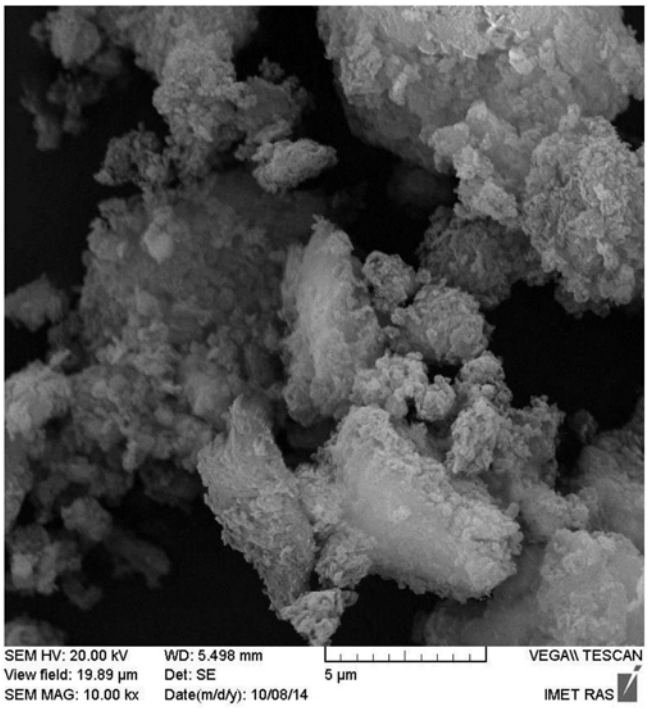

Figure 3. Electron micrograph of silica residue

It is found that filtration rate decreases exponentially with increasing of washing multiplicity (Figures 4 and 5). This can be explained by the fact that the residue with amorphous silica, which with reduced acidity of slurry and constant addition of fresh washing water transforms into gel [6] and reduces the permeability of the cake layer. Amorphous phase of silica covers the surface of large particles of Si-residue. The mechanism of alumina leaching with silica cage remaining suggested by some researchers was not observed. When this is seen, the layer thickness of filter cake decreases from 27 to 17 mm, i.e. increases its density and dehydration. Filtrate of the last washing step had almost neutral reaction (pH~7).

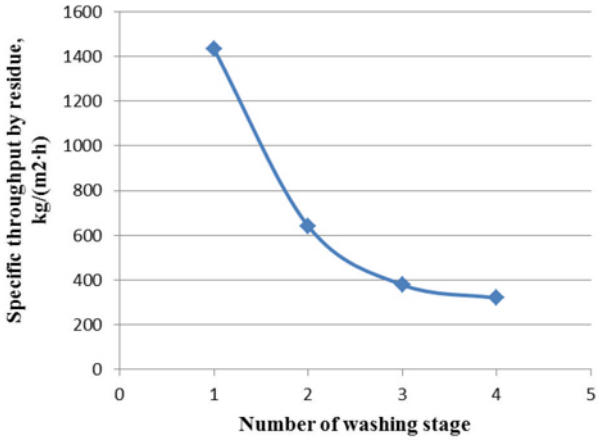

Figure 4. Parameters of filtration (solid phase)

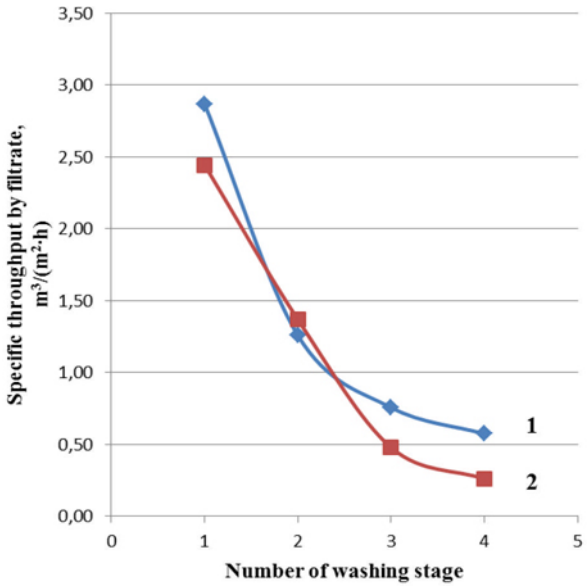

Figure 5. Parameters of filtration (liquid phase)

1- washing in fixed bed; 2 – reslurrying-filtration washing.

Maximum production rate of weak acid slurry filtration reaches 1434 kg/(m^2·h).

With pH=7 the filtering production rate of slurry expressed in filtrate (wash water) was only 2.87 m^3/(m^2·h). The same was in the silica residue washing mode in fixed bed – 2.44 m^3/(m^2·h).

The material of filtering partition (polypropylene cloth of filter paper) did not demonstrate notable impact on the process parameters as far as the limiting factor is the permeability of the washed silica residue layer.

It should be noted that on the fractures of silica residue layer the gravity segregation of particles is visually observed due to the horizontal location of filtering partition. In commercial press filters with vertical location of chambers this process is less visible and the productivity of filtration may vary.

6. Conclusions

1. Despite complex particle size distribution and mineralogical composition, silica residue after leaching of kaolin clay with hydrochloric acid may be filtered advantageously in a vacuum filter or press filter.
2. Average performance of slurry vacuum filtration under vacuum of 0.6 bar was 102.5 kg / (m^2 · h) by dry residue.
3. Maximum production rate of slurry filtration under pressure of 5 bar makes 1434 kg / (m^2 · h).
4. Due to higher production rate of filtration under pressure and to lower emissions of acidic vapors and aerosols at industrial implementation of the process using of press filter is preferable.
5. Cake washing rate with water on filter under pressure deteriorates with wash water acidity reduction, which can be explained by gelation of amorphous silica in the solid phase at values of pH, close to 7.
6. To choose the equipment design for washing additional tests are required.

7. Acknowledgements

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8. References

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