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## Study of the mechanism of pre-burned ash leaching by hydrochloric acid

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### ABSTRACT

The use of hydrochloric acid for processing aluminum-containing raw materials has a number of advantages over other acids, which include: easy decomposition of aluminum compounds with the transfer of aluminum into solution; low solubility of silica in HCl, the possibility of complete separation of the solid residue without significant losses of acid, etc. The paper considers the possibility of using the method for processing ash and slag dumps accumulated in large volumes in the country. Based on the thermodynamic analysis of reactions of interaction between ash components and hydrochloric acid, the behavior of aluminum, iron and nonferrous metal compounds during leaching is studied. It was shown that the preliminary roasting of ash with calcium chloride provides a high extraction of aluminum in the solution from the cinder. Based on experimental studies, the influence of time, temperature and acid consumption on the degree of aluminum extraction into the solution has been established. At optimal conditions of leaching conducted at S:L = 1:3, T = 60 °C,  $\tau$  = 60 min extraction of aluminum in a solution as chloride amounted to 99.92 %. At the same time the extraction of silica in solid sediment due to the maximum transfer of impurities in the solution was 99.8 %. The mechanism of the leaching process is proposed. The values of activation energy and the order of the reaction, indicating the complex 3-step character of the reactions, have been calculated. It is established that the limiting stage during leaching is the dissolution of anorthite.

**Keywords:** carbon black, leaching, hydrochloric acid, process mechanism, time, temperature, extraction, activation energy.

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## Introduction

Ash is the largest type of waste produced by large thermal power plants and steel mills as a result of coal combustion. More than 100 million tons of ash are produced in the U.S. each year. Annual ash output by developed country is, in million tons: India - 112, China - 100, Germany - 40 and UK - 15 [1, 2, 3].

In the Russian Federation there are more than 170 coal-fired thermal power plants, which burn 650 million tons of coal with the formation of 300 million tons of ash annually. More than 20 thousand km<sup>2</sup> of land plots are alienated for ash and slag waste storage in Russia, where 1.3-1.5 billion tons of ash are located [4].

In Kazakhstan, the annual output of ash and slag waste is about 19 million tons. To date, more than 300 million tons of waste has been accumulated in ash dumps [5]. In one major megalopolis in Kazakhstan, Almaty, more than 2 million tons of ash and slag waste have been accumulated as a result of three thermal power plants. Only during one heating season about 600 thousand tons of ash waste is added to the accumulated volumes of ash from coal combustion. The generated ash dumps have taken vast areas out of land use and have a negative impact on the environment (pollution of soil, air, groundwater).

The relevance and significance of the issues under consideration are enhanced with the fact that there is

no rational technology for ash processing. Significance of researches in the direction of development of highly efficient technology for ash processing consists in solving two key problems - ecological and technological. Solution of the first problem comes to involving the accumulated and current ash and slag wastes in processing and liberating large territories, and reducing the burden on the environment by reducing the volume of ash and its fine dispersion by the wind (20-40  $\mu$ ). Solution of the second problem ensures the use of ash as an additional source of raw materials with complex extraction of valuable metals with high added value.

The existing methods of ash processing [6, 7] allow extracting small amounts of valuable components. At the same time, according to the material composition ash can be considered as an independent complex raw material for the extraction of a whole range of metals [8, 9, 10]. Ashes compare favorably with conventional mineral deposits, they are located on the surface and do not require large expenses for extraction.

Positive research results [11, 12] allowed us to formulate a general concept of technology for the processing of ash of different chemical and mineralogical composition. Of particular interest is the application of the technology for the utilization of ash from small boiler plants, located within the boundaries of large cities and megacities.

The proposed technology can become an alternative for the production of alumina, silica and REM in countries where there are no bauxite deposits suitable for the production of alumina by the Bayer method and no natural sources for the production of pure silica and REM.

This paper presents the results of studies of the interaction of cinder components during its leaching with hydrochloric acid together with calcium chloride. Based on thermodynamic analysis of reactions of interaction between the components of the cinder with hydrochloric acid, the behavior of aluminum, iron and nonferrous metal compounds in the leaching process has been studied.

As a result of experimental studies, regularities of aluminum compounds dissolution during hydrochloric acid leaching depending on time, temperature, and hydrochloric acid consumption have been established. Optimal parameters of the leaching process providing maximum aluminum extraction into the solution as its chloride 99.92 % and high silica extraction into solid commercial sediment - 99.8 % have been determined.

### Research methods

The main methodological principle for studying the mechanism of ash leaching with hydrochloric

acid is the thermodynamic approach to the description of cinder leaching, which provides reliable determination of qualitative and quantitative characteristics of the formed complex composition solid (cinder) and liquid solutions of hydrochloric acid leaching.

Determination of the influence of hydrochloric acid consumption, temperature and time on the completeness of silica extraction into the commercial product in the form of precipitate and the maximum extraction of aluminum, nonferrous metals, REM and other associated elements in the solution was based on experimental results.

For the experiments a firing result, obtained under optimal burning conditions ( $T=1100$  °,  $\text{CaCl}_2$  consumption was twice higher than the required from stoichiometry for mullite decomposition,  $\tau=60$  min) of non-magnetic ash fraction together with calcium chloride, was used. The non-magnetic fraction of ash was obtained by magnetic separation of ash from a thermal power plant in Almaty [12].

The elemental and phase composition of solid and liquid products of cinder leaching with hydrochloric acid was performed using a D8 Advance analyzer (Bruker),  $\alpha$ -Cu, tube voltage 40 kV, current 40 mA. Processing of the obtained data of the diffraction patterns and calculation of the interplanar distances were performed using the EVA software. Sample interpretation and phase search were performed by Search/match using the PDF-2 powder diffractometer database.

In order to clarify and obtain reliable results of the phase composition of the initial cinder and leach products the X-ray diffractometric analysis on diffractometer DRON-3 with CuCa-radiation,  $\beta$ -filter was additionally performed. The diffractogram conditions:  $U=35$  kV;  $I=20$  mA;  $\theta=2\theta$ ; detector 2 deg/min. X-ray phase analysis on a semi-quantitative basis was performed on powder sample diffractograms using the method of equal weights and artificial mixtures. Quantitative ratios of crystalline phases were determined. Interpretation of the diffractograms was performed using the data from the ICDD: Powder Diffraction File (PDF2) and diffractograms of clean minerals. For the main phases the calculation of the content was carried out.

The total number of experiments ( $3k=9$ ) was determined based on the influence of two parameters on the required parameters, each of which was set in three levels:  $S:L = 1:2; 1:3; 1:4$  and temperature - 40, 60, 80 °C. 30 % HCl hydrochloric acid was used in the experiments. Initial weight of cinder in all experiments was 243 g. Time of cinder









<b>Total:</b>	<b>4863.04</b>	<b>100.00</b>	<b>66.98</b>		<b>100.00</b>	<b>286.24</b>		<b>100.00</b>	<b>338.07</b>		<b>100.00</b>	<b>5.40</b>		<b>100.00</b>
<b>Received</b>														
Precipitate	287.23	4.35	0.05	0.02	0.08	285.67	99.46	99.8	0.20	0.07	0.06	0.05	0.02	1.00
Solution	4575.81	95.65	66.93	1.46	99.92	0.57	0.01	0.2	337.87	7.38	99.94	5.34	0.12	99.00
<b>Total:</b>	<b>4863.04</b>	<b>100.00</b>	<b>66.98</b>		<b>100.00</b>	<b>286.24</b>		<b>100.00</b>	<b>338.07</b>		<b>100.00</b>	<b>5.40</b>		<b>100.00</b>

O			HCl			Прочие		
I	II	III	I	II	III	I	II	III
144.99	13.29	100.00				249.70	22.64	8.64
			1131.50	30.00	100.00	2640.16	70.00	91.36
<b>144.99</b>		<b>100.00</b>	<b>1131.50</b>		<b>100.00</b>	<b>2889.86</b>		<b>100.00</b>
						1.25	0.43	0.04
144.99	3.17	100.00	1131.50	24.73	100.00	2888.61	63.13	99.96
<b>373.22</b>		<b>100.00</b>	<b>1131.50</b>		<b>100.00</b>	<b>2889.86</b>		<b>100.00</b>

I – quantity, g; II – content, %; III – distribution, %

The yield of silica in the form of precipitate was ~26% of the weight of the cinder in the charge. The chemical composition of the pure silica obtained was, % (wt.): 99,5 SiO<sub>2</sub>; 0,02 Al; 0,07 Ca; 0,02 Fe.

The composition of the obtained mother liquor, g/l: 16.68 Al; 0.14 SiO<sub>2</sub>; 84.21 Ca; 1.33 Fe; 281.9 HCl; 0.004 Cu; 0.037 Zn; 0.001 Ni; 0.012 ΣREM; others.

High aluminum extraction into the solution was achieved - 99.92 %.

Extraction of silica into solid commercial product - 99.8 %.

### Conclusions

Based on the thermodynamic analysis of the reactions of interaction between the components of the cinder with hydrochloric acid, the behavior of aluminum, iron and non-ferrous metal compounds in the leaching process was studied.

As a result of experimental studies, regularities of aluminum compounds dissolution during hydrochloric acid leaching have been established depending on time, temperature, and hydrochloric acid consumption. Optimal parameters of leaching process providing maximum aluminum recovery into solution in a form of its chloride 99.92 % and high

silica recovery into solid commercial sediment - 99.8 % have been determined.

The mechanism of pre-burned ash leaching in hydrochloric acid has been established. It is shown, that the process speed is limited by anorthite dissolution and leaching of ash by hydrochloric acid proceeds stepwise in 3 stages in the temperature interval: at temperatures 20-40 °C - in the kinetic region (E<sub>a</sub> = 83.4 kJ/mol, n = 0.57), at 40-60 °C - in the intermediate region (E<sub>a</sub> = 53.12 kJ/mol), at 60-80 °C - in the diffusion region (E<sub>a</sub> = 32.34 kJ/mol, n ≈ 1).

**Conflict of interests.** On behalf of all authors, the corresponding author declares that there is no conflict of interest.

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**Алдын ала күйдірілген күлді тұз қышқылымен шаймалау механизмін зерттеу****Досмухамедов Н.К., Жолдасбай Е.Е., Даруеш Ғ.С., Арғын А.Ә., Құрмансейтов М.Б***Сәтбаев университеті, Алматы, Қазақстан*

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**ТҮЙІНДЕМЕ**

Құрамында алюминий бар шикізатты өңдеу үшін тұз қышқылын пайдалану басқа қышқылдармен салыстырғанда бірқатар артықшылықтарға ие, ол артықшылықтарға мыналарды жатқызуға болады: алюминий қосылыстарының ерітіндіге ауысып ыдырауының қарапайымдылығы; HCl-да кремнеземнің ерігіштігінің төмен болуы, қышқылды көп шығындамай қатты қалдықты толық бөліп алу мүмкіндігі және т.б. Жұмыста республика аумағында үлкен көлемде жинақталған күл-қож үйінділерін қайта өңдеу тәсілін қолдану мүмкіндігі қарастырылған. Күл компоненттері мен тұз қышқылының өзара әрекеттесу реакцияларын термодинамикалық талдау негізінде шаймалау кезінде алюминий, темір және түсті металдар қосылыстарының әрекеттері (таралуы) зерттелді. Күлді кальций хлоридімен алдын-ала күйдіру арқылы алюминийдің ерітіндіге жоғары дәрежеде бөлінуі қамтамасыз етіледі. Тәжірибелік зерттеулер негізінде ерітіндіге алюминийді бөліп алу дәрежесіне қышқыл шығынының, уақыттың, температураның әсері анықталды. Шаймалауды жүргізудің оңтайлы режимі жағдайында Т:Ж = 1:3, Т = 60 °С, τ = 60 мин. алюминийдің хлорид түрінде ерітіндіге бөлінуі 99,92% құрады. Бұл ретте қоспаларды ерітіндіге барынша максималды ауыстыру нәтижесінде кремнеземді қатты тұнбаға бөліп алу 99,8% болды. Жұмыста шаймалау процесінің механизмі ұсынылды. Белсендіру энергиясының мәндері және реакциялардың күрделі 3 сатылы сипатын көрсететін реакция тәртібі есептелді. Анортит еріген кезде шаймалаудың шекті кезеңі болатындығы анықталды.

**Түйін сөздер:** күйінді, шаймалау, тұз қышқылы, процестің механизмі, уақыт, температура, бөліп алу, активтендіру энергиясы.

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**Исследование механизма выщелачивания предварительно обожженной золы соляной кислотой****Досмухамедов Н.К., Жолдасбай Е.Е., Даруеш Ғ.С., Арғын А.А., Курмансейтов М.Б.***Satbayev University, Almaty, Kazakhstan***АННОТАЦИЯ**

Использование соляной кислоты для переработки алюминий содержащего сырья имеет ряд преимуществ по сравнению с другими кислотами, к которым можно отнести: простоту разложения соединений алюминия с переводом алюминия в раствор; низкую растворимость кремнезема в HCl, возможность полного отделения твердого остатка без существенных потерь кислоты и др. В работе рассмотрена возможность применения способа для переработки золошлаковых отвалов, накопленных в больших объемах на территории республики. На основании термодинамического анализа реакций взаимодействия между компонентами золы с соляной кислотой изучено поведение соединений алюминия, железа и цветных металлов при выщелачивании. Показано, что предварительный обжиг золы с хлоридом кальция обеспечивает высокое извлечение алюминия в раствор из огарка. На основании экспериментальных исследований установлено влияние времени, температуры и расхода кислоты на степень извлечения алюминия в раствор. В условиях оптимального режима ведения выщелачивания Т:Ж = 1:3, Т = 60 °С, τ = 60 мин. извлечение алюминия в раствор в виде хлорида составило 99,92 %. При этом извлечение кремнезема в твердый осадок за

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счет максимального перевода примесей в раствор составило 99,8 %. Предложен механизм процесса выщелачивания. Рассчитаны значения энергии активации и порядок реакции, указывающие на сложный 3-х ступенчатый характер протекания реакций. Установлено, что лимитирующей стадией при выщелачивании является растворение анортита.

**Ключевые слова:** огарок, выщелачивание, соляная кислота, механизм процесса, время, температура, извлечение, энергия активации.

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