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ИЗВЕСТИЯ

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РЕСПУБЛИКИ КАЗАХСТАН

АО «ИНСТИТУТ ТОПЛИВА, КАТАЛИЗА И
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ХИМИЯ ЖӘНЕ ТЕХНОЛОГИЯ СЕРИЯСЫ

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СЕРИЯ ХИМИИ И ТЕХНОЛОГИИ

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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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METHODS FOR EXTRACTION OF VALUABLE COMPONENTS FROM ASH-AND-SLAG COAL WASTES

Abstract. In the article the problems of ash and slag wastes processing, which are formed from coal combustion in CHP, are considered. General information is given on the chemical composition of ash and slag wastes and the content of valuable components of the most developed and used deposits in Kazakhstan and attractive from the point of view of extracting valuable materials from them. Among such deposits are the Karaganda basin, the Ekibastuz basin, the Maikuben basin, the Borly field, and the Kara-Zhyra field.

The literature review of the methods of leaching the elements from ash and slag waste from coals showed that the conditions of the process and the selection of the necessary reagents depend on the composition and the degree of preparation of the initial coal ash, and the concentration of the extracted component is an important component.

The most common and effective methods of extracting valuable components from ash are leaching with acids and alkalis. However, the use of such expensive reagents already in the production of these products requires the careful development of an appropriate technology (across the entire process chain), where it is also possible to recover the reagents. In addition, despite the relatively high degree of extraction of microelements, acid leaching has disadvantages associated with the use of expensive acid-fast processing equipment and the difficulty of separating siliceous sludge from acid solutions of salts and the difficulty of purifying aluminum salts from iron.

Promising technologies for extracting valuable components from ash are biochemical heap leaching with the use of thiobacteria Th. Ferrooxidans, fluoride technology (using fluorine and hydrogen fluoride, or fluoride and ammonium bifluoride).

Keywords: coal, ash, leaching, acid, alkali, metals, recovery, macroelements, microelements.

Introduction. Recently, more attention has been paid to environmental issues related to the development of technology and technology in Kazakhstan. In this regard, an integrated approach to solving the problems of utilization of various wastes has become relevant, including ash and slag.

Each year, a huge amount of ash and slag wastes are generated at the thermal power station, and the largest producers are China, the United States and India (table 1) [1].

The current global annual production of ash and slag is approximately 750 million tons [2], and in the near future, this amount of waste is expected to grow. This fact is one of the serious environmental problems associated with the threat to public health and environmental safety (damage to soil, plants, atmosphere). Fly ash can even get into the soil and contaminate groundwater with heavy metals [3, 4]. In this regard, there is a necessary need for the utilization and processing of ash [5].

As the Head of State N. Nazarbayev noted in his message to the people of Kazakhstan on January 10, 2018: "It is important to increase the requirements for energy efficiency and energy saving of enterprises, as well as the environmental friendliness and efficiency of the energy producers themselves.

Table 1 - Annual production of coal ash in the world (2013)

Country	Ash production (mln. tons)
China	385
USA	118
India	105
Europe	52,6
Middle East and Africa	32,6
Russia	26,6
Asia	16,7
Australia	13,1
Japan	11,1
Canada	6,8

At present 500 million tons of ash and slag waste has accumulated in the Kazakhstan, and this volume is growing by 19 million tons per year. At the same time, ash dumps occupy large areas, and their construction requires significant capital expenditures from power plants, which ultimately affect the cost of production of energy(according to the Kazakhstan Electric Power Association)..

From ash-and-slag wastes from coal produced by CHP, about 8% of ash is processed in Kazakhstan (less than 1.9 million tons). If the use of ash remains at this level, by 2020 the amount of accumulated waste will exceed 650 million tons, and by 2030 - 1 billion tons [6].

In this context, global processing of ash not only contributes to the improvement of the ecological state of the environment, which is a priority, but additionally (except for energy) will significantly improve the efficiency of coal processing with the production of high added value products.

Ash-and-slag wastes have specific properties that determine the possibility of their effective use in various industries. A wide application of processing of ash and slag wastes was found in the developed countries of the West, where about 65-70% of ash and slag (formed by heat and power plants) are processed, mainly in the production of building materials (as additives in cement, concrete, bricks, etc.). In Germany, Denmark, China, up to 100% of the annual output of ash and slag materials is used in the production of building materials. In Germany, it is currently forbidden to build coal-fired power plants and ash-and-slag-dumps without the technology of 100% processing into other goods. Changes in Indian law led to an increase in the use (utilization) of ash from 30% of the annual output to 53%, which is about 70 million tons/year [6].

At the same time, in addition to building materials, various valuable metals can be obtained from ash and slag wastes. Many rare elements found in ashes are in demand and are intensively used, for example: yttrium - for the production of new structural and high-temperature superconducting ceramics and phosphors; scandium - in military technology, for the manufacture of halogen lamps; Lithium - for the production of aluminum-lithium alloys for aircraft missile technology; gallium - for the production of laser diodes for fiber-optic communication and ultra-high-frequency radar equipment; beryllium - in electrical engineering and electronics, in aerospace engineering, in the automotive industry; germanium - for the production of infrared technology, fiber optics, in pharmaceutics, in metallurgy.

Chemical composition of ash-and-slag wastes

The composition of ash and slag wastes is determined by the mineral composition of the coals, which depends on the deposit, the depth of the beds, methods of extraction and enrichment, and the ash content of the coal is constantly increasing.

The chemical properties of ash and slag waste vary greatly depending on the type of coal, combustion temperature, combustion technology, air/fuel ratio and coal particle size. The main part (up to 98-99%) of ash and slag wastes are compounds of ash-forming macroelements (Si, Al, Fe, O, Ca, Ti, Mg, S, K, Na). The remaining elements (microelements) are present in the ash at a level of 0.1% or less. Some of the trace elements (Sr, Ba, Sc, Y, La, Ti, Zr, etc.) are contained in the slag. Other elements (Ga, In, Tl, Ge, Sn, Pb, etc.) at temperatures above 1000 0C are removed from the high temperature zone and condense in cyclones, electrostatic precipitators (at 110-120 °C) [7].

Alkali and alkaline-earth metals (Na, K, Ca, Mg, etc.) occupying the position between macro and micro components are in the form of organomineral components, and also form inorganic compounds (calcite, dolomium, gypsum).

All elements of ash can be a part of both the mineral part of the coals (i.e., form minerals) and in the form of compounds with organic matter of coals, forming so-called organomineral components, which are the least studied forms. These include: salts of humic acids (K, Na, Ca, Mg, etc.), complex humates characterized by a cyclic system of bonds, as well as elementorganic compound compounds (ie, with a bond C-E, where E - S, Si etc.).

Phase-mineralogical composition of ash is determined by compounds of inorganic components in coal, as well as by physicochemical processes occurring during coal combustion. The main quantity of inorganic elements is concentrated in the form of quartz, minerals of the kaolinite group, siderite (FeCO3). As admixtures there are hydromicas, feldspars, calcium carbonates (aragonite CaCO3 and calcite CaCO3), magnesium (magnesite MgCO3), pyrite (FeS2). The content of iron varies considerably in coals, the main compounds of which are siderite and pyrite, which sometimes form quite large concretions.

The problems of the origin and distribution of basic inorganic components in coals and their processing products are described in works [8, 9].

In some coal deposits (as in ores), there are elevated concentrations of valuable metals - vanadium, germanium, titanium, tungsten, zirconium, gallium, niobium and some others. Thus, up to 40-67% of titanium, 45-77% of beryllium, 70-87% of copper, 50-81% of manganese, 74-84% of arsenic, 48-60% of vanadium and 62-83% of gallium are extracted from ash-and-slag wastes of brown coal.

Thus, a significant accumulation of ash and slag wastes due to burning of coals is the reason for special attention to the study of the chemical composition of coals with the further development of technologies for extracting valuable elements from ash. We will briefly review the physicochemical composition of the coals most used in Kazakhstan and attractive from the point of view of extracting valuable substances from them (data are taken from [10]).

*The Karaganda basin (hard coal).*The coal ash is refractory (melting point 1250-1500 ° C). In separate layers (Dolinskaya and Tentekskaya suites), the yttrium content reaches 40-54 g/t ash, scandium up to 43 g / t ash.

Karaganda basin (brown coal). Low-sulfur coals (0.5-0.8%), medium phosphorus (0.01-0.08%).Coals of the Dubov suite are characterized by increased concentrations of yttrium (up to 180 g/t of ash), scandium (up to 90 g/t) and other impurity elements (beryllium, vanadium, chromium, cobalt).

Ekibastuzsky basin. It is one of the coals most used at CHP. The actual average ash content of coal is 39%. The ash of the top three layers is refractory (1610-1690 ° C), highly abrasive. Coals are low-sulfur (0.4-1.0% S total, with predominantly organic sulfur), polyphosphorous. A peculiar feature of the ash of Ekibastuz coals is the increased content of alumina (26-30%). In heavy fractions with a density of more than 1.7 g/cm^3, zinc, copper, lead, and also silver, scandium and other elements are concentrated to a few hundredths of a percent. Calculations showed that from the ash yield of about 30 million tons, with the creation of the appropriate technology, it is possible to extract 70,000 tons of titanium, 24,000 tons of zinc, 12,000 tons of lead, 9,000 tons of tin, 3,000 tons of copper, 180 tons scandium, 30 tons of silver and other elements (vanadium, manganese, zirconium). Considering the huge reserves of ash and slag waste obtained from the burning of Ekibastuz coals at the CHP, the issue of extracting valuable components from them can become an important economic problem. Then, ash waste can be used as raw material for building materials.

Maykubensky basin. Coals of the basin are humus, brown with a high degree of coalification, medium-ash. The ash is refractory, with a high content of Al2O3 (up to 30%). Coals are low-sulfur (0.5-1.0%) and polyphosphorous (0.1%).

In addition, elevated scandium concentrations (up to 0.05%, an average of 7 clarkes), yttrium (up to 0.03%), ytterbium (up to 0.005%, an average of 10 clarkes), gallium and zirconium (up to 0.06%) arein the coal ashes of the Shoptykol suite. High concentrations are characteristic for copper, zinc and lead. The titanium content reaches 1%. It is noted up to 100 g of beryllium per 1 t of ashe, 1-30 g/t of silver.

The ashes of Maykubensky coals with a high Al_2O_3 content can be a good raw material for alumina production. In addition, the ash from the coals of the Shoptykol suite is a complex raw material not only for the production of aluminum, but also for titanium, scandium, rare earth elements and other valuable impurity elements. In addition, the presence of biostimulants (phosphorus, boron, zinc, etc.) in the ashes allows them to be used as microfertilizers.

The Borlydeposit. Coals are humus, stone, high-ash (32-40% and more), low-sulfur. Ash is characterized by a high content of alumina (an average of 26.8%). The elevated Al_2O_3 contents (38-39%) are characteristic in particular of the coals and rock layers of the lower coal horizon. The same coals are characterized by fairly high concentrations of titanium (3400 g/t in coal and 8,500 g/t in ash), zirconium (209 and 520 g/t in coal and ash, respectively), yttrium (25 and 62 g/t), ytterbium (2.5 and 6.5 g/t) and scandium (209 and 520 g/t).

The Kara-Zhyradeposit (the old name is Yubileynoye). Coals belong to the brown (B3) high-metamorphosed, transitional to the stone long-flame, humic with an ash content of 14-19% (average 16.3%), low-sulfur (average sulfur 0.48%).Coal ash, in addition to titanium, is enriched with scandium (46-95 g / t ash), yttrium (66-79 g / t ash), beryllium (more than 10 to 50 g / t ash), copper (the vast part contains 100-300 grams / t ash) and other elements-impurities. On a large area of coal seams, the concentrations of these elements are maximal. Taking this into account, the coals of the deposit should be considered as a potential source of rare-earth-scandium raw materials and more detailed additional research is needed.

Some basic indicators of the chemical composition of the above coals are summarized in Table 2 (the gold-forming organic and mineral macroelements C, H, S, P, Si, Al, Fe, O, Ca, Ti, Mg, K, N are given in units of mass% microelements Ti, Zr, Sc, Y, Yb are given in units of - g/t ash, A^r- ash content of coal, W^r_t-coal moisture, T_m - melting temperature of ash).

Table 2 − Chemical composition of Kazakhstan coal [10]

The Karaganda basin (hard coal)

A^r	T_m^2	SiO_2	Al_2O_3	CaO	MgO	SO_4
от 10-15 до 25-40	1250-1500 ^{0}C	51	35	7	1	4

The Karaganda basin (brown coal)

W^r_t	A^r	S	P	C	H	Y	Sc
17-25	16-21	0,5-0,8	0,01-0,08	71	5,4	до 180	до 90

Ekibastuz Basin

A^r	T_m	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	N_2O	K_2O	Ti	Zr	Y
39	1610-1690^{0}C	62,9	28,6	3,8	1,1	0,3	2,4	0,2	до 10000	до 10000	30

Maykubensky Basin

A^r	S	P	Al_2O_3	Sc	Y	Yb	Zr	Ti	Be	Ag
25-28	0,5-1,0	0,1	до 30	до 0,05	до 0,03	до 500	0,06	до 10000	100	1-30

The Borly deposit

A^r	Al_2O_3	Ti	Zr	Y	Yb	Sc
32-40	38-39	8500	520	62	6,5	520

The Kara-Zhyra

A^r	S	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	SO_3	Sc	Y	Be
14-19	0,48	45,7	29,8	8,25	5,01	1,2	2,06	5,63	46-95	66-79	10-50

Methods of extraction the elements from ash and slag wastes

- In studies devoted to the study of the leaching of trace minerals, the experiments differ in both the set of elements studied (depending on the qualitative composition of the ash), the choice of the reaction medium for leaching, and the temperature and time treatment regimes. Analysis of literature data on how to extract trace minerals allows them to be divided into three main groups:
- acid methods. For the extraction of microelements of basic and amphoteric character, solutions of strong mineral acids (H_2SO_4, HC1, HNO_3) [11-13], acetic acid [13] are used;

– alkali methods. Alkaline solutions (NaOH, Na_2CO_3, $NaHCO_3$, NH_4OH) [12], $Ca(OH)_2$ are used to extract microelements of acidic and amphoteric character [14].

– extraction in harsh process conditions (increased pressure, temperature) [15] or with use of aggressive media (oxidation-reduction or chlorinating calcination) [16], fusion with chlorides, sublimation [17];

– biotechnology of metal leaching (using bacteria) [18].

In addition, recently, the fluoride methods of processing mineral raw materials have been increasingly developing. Previously, fluorides were used, mainly, for the production of uranium hexafluoride in the nuclear industry. Fluoride technologies allow expanding the range and depth of extraction of elements. The condition for the profitability of fluoride technologies is the use of fluorine and hydrogen fluoride in pure form, or in the form of more technological fluoride and ammonium bifluoride [19]. The method of fluoride processing of ash consists in the fact that hydrogen fluoride interacts with the ash and transfers silicon (contained in the ashes) to the gaseous compound - tetrafluorosilane. This separates the silicon compound from the bulk of the substances. Tetrafluorsilane is absorbed with a solution of ammonium fluoride, which is then treated with an excess of ammonia to isolate the highly dispersed residue. The physicochemical basis of this process with the use of ammonium fluorides is the difference in the properties of ammonium fluorometallates. For the complete extraction of components from the ash, optimal process conditions are determined by varying the difference in the physicochemical properties of ammonium fluorides and fluorometallates [20].

Prior to direct leaching of valuable components from ash, unburned coal (undersized) and iron-containing fractions are usually recovered. Unburned (content in ash is 5-15%) is separated from the ash usually by the froth flotation method (on flotation machines). With regard to trace elements, separation of coal will further increase their content in the solid residue. The most common method of magnetic separation is used to separate the iron-containing fraction from the ash. In addition, there is an additional stabilization of the composition of macrocomponents.

The complex processing of fly ash from the Ekibastuz Basin is proposed in the work [21], the technological scheme of which is shown in Figure 1. Such processing includes sulfuric acid leaching of rare-earth and radioactive metals, followed by alkaline extraction of gallium and amorphous silicon oxide.

Aluminium extraction

In accordance with the reagents used, the sintering processes can be separated into lime or calcination agglomerate, the Kalsinter process and other agglomeration processes. The agglomeration processes include a high temperature reaction of coal fly ash with powdered sintering agents to form soluble alumina compounds. The agglomerate is then leached (to separate aluminum) and the resulting solution is treated to produce high purity alumina.

In the agglomeration process, the ash reacts with lime (added as limestone) at an elevated temperature (> 1100 ° C) to form calcium aluminate (soluble in the extractant) and calcium silicate insoluble in the same solution. The extraction of alumina from the agglomerate is carried out by dissolving the alumina in the extractant and precipitating the calcium silicate as a solid residue. Conventional extractants include water and dilute alkaline solutions, such as Na_2CO_3 and NaOH [22]. After leaching, aluminum precipitates as $Al(OH)_3$ by contacting the solution with CO_2. The next step is calcining the precipitate to produce the final product of α- or γ-alumina.

The first method of agglomeration with calcareous soda was developed by Kaiser A. in 1902 to separate alumina from silica. It is known that the reaction of a mixture of lime and soda with fly ash forms soluble sodium aluminate and insoluble calcium silicate. At high temperatures (usually 1100-1400°C), the formation of other compounds is inevitable, depending on the type of fly ash and sintering conditions. As in lime agglomeration, the sintered product is leached with water, caustic soda or sodium carbonate solution. Therefore, the agglomeration process with calcareous soda also includes a purification step of the solution. The resulting suspension is filtered and the solution is treated with $Ca(OH)_2$ suspensions to precipitate the dissolved silica at a high temperature and pressure, which is then decomposed in the same manner as in the Bayer process, or treated with CO_2 to precipitate the hydrated alumina. $Al(OH)_3$ is separated and converted to alumina by calcinations.

Wang and co-authors [23] extracted aluminum by pre-precipitation of fly ash, agglomeration with lime and soda, dissolution and carbonization. The degree of recovery reached 40%, and the Al_2O_3/SiO_2 molar ratio increased after preliminary precipitation. The rate of extraction of alumina from the agglomerate reached 91%.

Bai and co-authors [24] extracted alumina from the precipitated fly ash by the agglomeration process with lime and soda. The extraction rate reached 90% under optimal conditions. Bai and co-authors [25] obtained aluminum from fly ash by dilution with alkali and carbonization to convert amorphous silica to a product of amorphous nanoparticles. In this process, fly ash is mixed and sintered with gypsum and limestone at a temperature of about 1000-1200°C. The agglomerate is then leached with dilute acid. The solid waste particles are removed by filtration, and the metal residues are recovered from the filtrate.

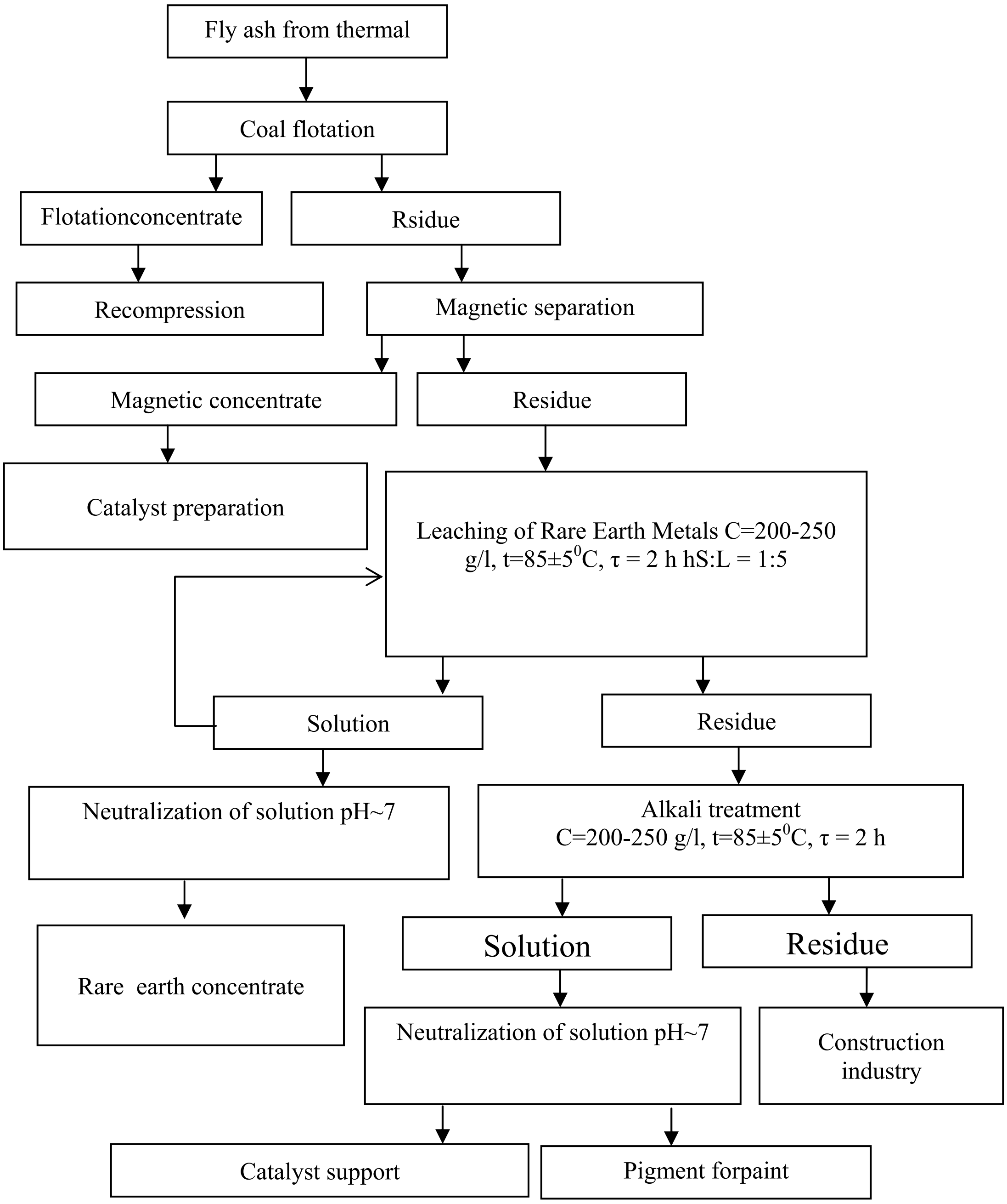

Figure 1 – Technological scheme of complex processing of fly ash from the Ekibastuz basin

In the patent [26], fly ash was sintered with a mixture of NaCl and Na_2CO_3 at temperatures of 700-900°C. The agglomerate was then leached with nitric or sulfuric acid, recovering 90-99% aluminum. The careful separation of aluminum from silicon can be achieved by a direct acid leaching process. Usually, sulfuric, hydrochloric and nitric acid is used to leach fly ash. An aqueous suspension of 20% (w/v) fly ash is prepared using 16 mol/l HNO_3 and 36 mol/l H_2SO_4, which will dissolve no more than 10% of the total amount of aluminum at ambient temperature for 72 hours. A greater amount of aluminum is recovered by leaching under reflux conditions for a long period of time; and even then not more than half of the aluminum is dissolved in the acid filtrate.

Wu et al. [27] extracted aluminum from fly ash by acid pressure leaching. The optimum conditions were determined: sulfuric acid concentration 50% and reaction temperature 180 ° C for 4 hours. Under optimal conditions, the extraction efficiency reached 82.4%. In comparison with traditional heating processes, microwave heating has its advantages, since it can be selective, controlled and effective.

In [28, 29], alumina was extracted using the acid sintering leaching process. A mixture of fly ash and concentrated sulfuric acid was calcined to convert most of the aluminum to aluminum sulphate, which can be extracted with hot water. The degree of extraction of aluminum oxide reaches 70-90% with a relatively lower processing temperature and a smaller amount of solid residue.

In [30], fly ash was calcinated with soda at 900 ° C to obtain soluble aluminates. The agglomerate was then leached with sulfuric acid to produce a solution containing aluminum. The recovery efficiency reached above 98%.

In [31], high-temperature chlorination of fly ash was studied using a reactor with a gas-liquid layer. In the presence of carbon and carbon monoxide present as reducing agents, about 25% of the alumina in the ash was chlorinated for 2 hours at a temperature above 900 ° C.

Извлечение Sc, Y, La

In [32] scandium, yttrium and lanthanum were leached from the ash. An aqueous solution was prepared in a ratio of solid and liquid phases of 1:10 (10 g of ash and 90 ml of distilled water). The following acids were used: sulfuric acid H_2SO_4 - 93.6-95.6% by weight. (GOST 4204-77); nitric acid HNO_3 - 65% by weight (GOST 4461-77); Hydrochloric acid HCl - 35% by weight (GOST 3118-77). After acid addition, the samples were placed in a shaker for 0.5 hours, or 2.5 hours at 80 ° C and 250 rpm. As a result, it was found that the optimal leaching conditions are as follows: for lanthanum - 25 g HNO_3, T = 80 ° C, t = 2.5 hours (average leaching value 49.5%); for yttrium - 5 g H_2SO_4, T = 80 ° C, t = 2.5 hours (average leaching value 45.33%); for scandium - 5 g H_2SO_4, T = 80 ° C, t = 2.5 hours (average leaching value 75%). It can be seen that the most effective treatment is sulfuric acid treatment and leaching at 80 ° C for 2.5 hours.

The authors of work [33] extracted yttrium and scandium from the ash of brown coals with hydrochloric acid solutions. The optimal leaching conditions were established: T = 40-50 ^{o}C, the initial concentration of HCl was 2.5-3.2 mol/l, the ratio of T: F = 1: 4-1: 5, the duration of the process was 30-60 min. At the same time, 95-96% of yttrium and 85-90% of scandium pass into the solution, which is a rather high index.

Extraction of aluminum and titanium

The method for reducing Al and Ti involves leaching fly ash by acid / alkaline leaching, followed by precipitation, solvent extraction or recrystallization [34-36].

An acid pressure leaching method was demonstrated in [37], in which high extraction (82.4%) of Al was obtained by reducing the size of fly ash (74 μm) and increasing the acid concentration (50%). However, in this method, non-target metals were easily leached into the acid, which led to contamination.

Extraction of vanadium

In the patent [38] used an acid solution for the recovery of vanadium V. Extraction was carried out by precipitation of vanadium pentoxide as a result of increasing the pH by adding calcium hydroxide, lime or calcium carbonate to the acid solution. After precipitation of vanadium V, the solid was separated by filtration or centrifugation. The recovery percentage of V from the acidic solution was ≥ 98%.

An acid leaching process using large volumes of sulfuric acid was also described in ref. [39], where the recovery of vanadium V was up to 95.8% from the filtrate.

Extraction of silicon and gallium

In the hydro-alkali treatment of fly ash from Ekibastuz coal, silicon and gallium were recovered [40]. Under optimum conditions (T = 85 ± 5 ° C, t = 1 h, C_w = 200-250 g / l, T: F = 1: 4-6), the recovery of silicon (based on SiO2) is 49.3%, aluminum - 5.5%, gallium - 56%. The leaching solution is characterized by the following parameters: SiO_2 - 60 g/l, Ga - 5 mg/l. For the subsequent extraction of gallium, known schemes can be used, including extraction or ion exchange. Amorphous silicon dioxide can be isolated from the solution and used as a raw material for the chemical industry, for example, to obtain a silicate matrix of catalysts, paint and varnish, white soot.

Extraction of gallium and germanium

After the combustion of coal at the power plant, the fly ash is enriched with gallium Ga and germanium Ge in comparison with the initial coal [41].

The extraction of Ge and Ga from the ash was carried out using various extractants in a wide range of extraction conditions (acidic, alkaline, complex, reducing and oxidizing) [42]. High extraction yields of Ge (up to 90%) and Ga (up to 82%) were obtained using weak solutions of oxalic and sulfuric acids, respectively, for 1-2 hours of the extraction period.

In order to extract Ge germanium from solution, an ion flotation method using various complexing agents (pyrogallol, catechol, hydroquinone and resorcinol) in the pH range 4-7 was developed in Ref. [43]. It was found that when dodecylamine is used as a surfactant and pyrogallol or catechin as a complexing agent at pH values of 4-7, germanium can almost completely be recovered in 30 minutes. The use of catechol as a complexing agent for the extraction of Ge (from filtrates) was also noted in [44].

Extraction of aluminum, gallium and germanium

A special place is occupied by works connected with bacterial leaching of microcomponents from ash [45,18]. The basis of this process is the oxidation of sulfide minerals, which are contained in rocks. Thionic bacteria oxidize the sulphides of iron, copper, zinc, etc. At the same time, metals from an insoluble sulphide form transform into sulphates that dissolve well in water. From sulfate solutions, metals are extracted by extraction, sedimentation, sorption.

Monograph [18] developed a schematic diagram of bacterial (biochemical) leaching of aluminum, gallium, and germanium by Thion bacteria Th. Ferrooxidans by the method of biochemical heap leaching from the coal mine dump. The process of metal extraction consists of such operations: selection of an industrial site and its preparation for heap leaching; preparation of waterproofing base; ore preparation; installation of pipelines, sump, sedimentation tanks and collectors; delivery and storage of the rock; irrigation of ore dumps with ready-made bacterial solutions; directly the process of bacterial leaching of metals; drainage of the solutions through a heap pile; accumulation of metal solutions in sedimentation tanks and reservoirs; delivery through the pipeline system of the formed solution with metals to the processing complex for processing the obtained solutions and obtaining the chemical concentrate of the extracted metal.

Extraction of cerium, gallium, vanadium

In the works of the Department of Inorganic Chemistry, Omsk State University, the possibility of extracting rare and rare-earth elements from the ash of Ekibastuz coals was studied [46]. When the ash is treated with sulfuric acid (C = 200 g/l, t = 2 h, T: L = 1: 5), the recovery rates of rare metals are small: Ce - 0.35%, Ga - 1.2%, V - 4 , 6%. Increasing the temperature to 85^oC increases the recovery of these metals to 82; 16.3; 5.8% respectively. An effective method is the addition of NaCl. The use of a sulfuric acid solution (C = 200 g/l) with a NaCl concentration of 50 g/l at 85 ° C makes it possible to extract 90% of Ce from the ash, while Ga extraction was 25.6%, V = 7%. When coal ash is treated with sulfuric acid, radioactive elements - uranium and thorium - also leach out of it. Under these conditions, the recovery rate is 87% for uranium, 86% for thorium. Increase the recovery of rare earth elements from ash in the sulfuric acid medium by electrochemical leaching.

The extraction of REE

The elements of rare earth metals include light REE (Sc, La, Ce, Pr, Nd and Pm), average REE (Sm, Eu and Gd) and heavy REE (Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), which are mainly used for various industrial purposes, such as fuel cells, high capacity accumulators, magnets for wind generation[47-49].

There are several methods developed to extract rare elements from ash. The method of chlorination is preferable because of its selectivity and high reactivity, but this method is expensive. This method can be used to recovery only some rare elements, where other complex recovery processes are not suitable.

The patent [50] describes the reduction of REE from ash. In this method, the ash samples were first treated with mineral acid (HNO3) at 90 ° C to form a more concentrated mineral acid solution. This solution was mixed with an organic solution (tributyl phosphate and kerosene), which includes salts of rare earth metals. The organic solution was mixed with water to form an aqueous solution of REE and the REE was recovered using an ion exchange process.

Conclusions

The methods of extracting useful components from ash and slag wastes considered in this paper are mainly used in laboratory conditions. Therefore, the commercialization of these methods and their introduction on an industrial scale is one of the most important technological and environmental problems in Kazakhstan. A processing of ash in construction materials and valuable components, for example, near (in the territory) CHP, as well as numerous boiler houses, can significantly increase the efficiency of their operation, as a result, it will significantly reduce the cost of produced heat and / or electricity. In addition, the industrial production of these products (in addition to increasing local workplaces) will lead to a significant reduction (or lack, depending on the volume of production) of the volume of the corresponding imported products.

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КӨМІР ШЛАК ҚАЛДЫҚТАРЫНЫҢ ӨНІМДЕРІНЕН БАҒАЛЫ КОМПОНЕНТТЕР АЛУДЫҢ ӘДІСТЕРІ

Аннотация. Мақалада ЖЭС да көмірді жағу барысында шығатын күл шлак қалдық тарын (КШҚ) қайта өңдеу мәселелері қарастырылды. Шлак қалдықтарының жалпы химиялық құрамы, құрамындағы бағалы қоспалардың сонымен қатар Қазақстандағы меңгерілген және пайдаланылатын кен орындарында бағалы заттарды алу жайлы мәліметтер берілді. Осындай кен орындар ретінде Қарағанды бассейні, Экібастұз бассейні, Майқұбы бассейні, Борлы кен орыны, Қара-Жыра кен орындары таңдалды.

Көмір шлак өнімдерінен элементтерді шаймалау жайлы жасалған әдеби шолуда іс жүргізу жағдайы және де қажетті рективтерді таңдау көмір күлінің бастапқы дайындау дәрежесі мен құрамына байланысты, ал басты құрамдас факторы болып алынатын компоненттің концентрациясы болып табылатыны анықталды.

Көмір шлак қалдықтарының күлінен пайдалы компоненттерін алуды жүзеге асыру үшін көбінесе таралған және тиімді әдістер ретінде қышқылдық және сілтілік шаймалау болып табылады. Біракта мұндай қымбат реагенттерді осы өнімдерді шығару барысында қолдану мұқият қажетті технологияларды әзірлеуді талап етеді, сонымен қоса реагенттерді қалпына келтіру мүмкіндігі де болуы қажет. Микроэлементтерді алынудың жоғарғы деңгейіне қарамастан өз кемшіліктері де бар, қышқылдық шаймалау қымбат қышқылға төзімді технологиялармен байланысты қондырғыларды қолдану, кремнийлі шлакты тұз қышқыл ерітінділерінен ажырату және алюминий тұзынан темірді тазарту сияқты қиыншылықтары бар.

Шлак қалдықтарының күлінен бағалы компоненттерді алу үшін келешегі бар технология болып биохимиялық үйме шаймалау болып табылатын Th. Ferrooxidans тиондық бактериялар, фторлық технология (фтор және фторсутекті немесе фторид және аммоний бифторидін) қолдануға болады.

Түйін сөздер: көмір, күл, шаймалау, қышқыл, сілті, металлдар, қайта қалпына келтіру, макроэлементы, микроэлементы.

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МЕТОДЫ ИЗВЛЕЧЕНИЯ ЦЕННЫХ КОМПОНЕНТОВ ИЗ ЗОЛОШЛАКОВЫХ ОТХОДОВ УГЛЕЙ

Аннотация. В статье рассмотрены проблемы переработки золошлаковых отходов (ЗШО), образующихся от сжигания угля в ТЭЦ. Приведены общие сведения о химическом составе золошлаковых отходов и содержании в них ценных компонентов некоторых наиболее освоенных и используемых в Казахстане месторождений и привлекательных с точки зрения извлечения из них ценных веществ. Среди таких месторождений выбраны Карагандинский бассейн, Экибастузский бассейн, Майкубенский бассейн, месторождение Борлы, месторождение Кара-Жыра.

Проведенный литературный обзор методов выщелачивания элементов из золошлаковых отходов из углей показал, что условия ведения процесса и подбор необходимых реактивов зависят от состава и степени подготовки исходной угольной золы, а важным составляющим фактором является концентрация извлекаемого компонента.

Наиболее распространенными и эффективными методами извлечения ценных компонентов из ЗШО является выщелачивание кислотами и щелочами. Однако использование таких дорогостоящих реагентов уже в самом производстве данных продуктов требует тщательной разработки соответствующей технологии (по все цепочке процессов), где имеется возможность еще и восстановления реагентов. Кроме того, несмотря на относительно высокую степень извлечения микроэлементов кислотное выщелачивание имеет недостатки, связанные с применением дорогостоящего кислотоустойчивого технологического оборудования исложностью отделения кремнеземистого шлама от кислых растворов солей и трудностью очистки солей алюминия от железа.

Перспективными технологиями извлечения ценных компонентов из ЗШО является биохимическое кучное выщелачивание с применением тионовых бактерий Th. Ferrooxidans, фториднаятехнология (с использованием фтора и фтороводорода, илифторида и бифторида аммония).

Ключевые слова: уголь, зола, выщелачивание, кислота, щелочь, металлы, восстановление, макроэлементы, микроэлементы

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