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PROCESSING OF ASH AND SLAG WASTE

Abstract. This article is dedicated to the identification of perspective areas for the disposal of ash and slag waste from thermal power plants, namely waste generated at the TPP-1 in Pavlodar. The composition of ash and slag waste was considered by methods of X-ray fluorescence and X-ray phase analysis in order to identify the most suitable area for their further use. Based on the data obtained, it was proposed to use waste for the extraction of precious metals, such as aluminum and iron, by alkaline leaching. The paper presents the results of selection of the most optimal conditions (temperature, alkali concentration, duration of the process) leaching of metals. It was found that the best conditions for the extraction of iron is the treatment of ash and slag waste in an alkaline environment of caustic soda with a concentration of 200 g / l at a temperature of 80 °C for 3-4 hours. To increase the degree of aluminum extraction, it is necessary to apply repeated treatment with an alkali solution, consisting in sequential treatment of ash and slag waste with fresh alkali solutions in 3 stages for one hour.

Key words: industrial waste, ash and slag waste, metals, leaching, disposal.

Introduction. Coal, as the main energy in the world, will produce large quantities of waste slag after incineration and gasification, which is considered a type of solid waste [1] and can be recycled as a secondary resource by acidification [2]. However, this material, due to its enrichment with volatile pollutants and heavy metals [3], is quite hazardous. The increased content of heavy metals in ash and slag waste can create problems when handling such residues due to their potential risk to the ecosystem [4, 5]. Moreover, in comparison with their total concentrations, the toxic effect of hazardous metals is largely determined by their speciation [6, 7].

Huge amounts of industrial by-products such as copper and blast furnace slag, fly ash, coke ash, etc. are generated all over the world and cause serious problems with their environmentally sound disposal.

Currently, there are many methods allowing the disposal of ash and slag waste, but in practice, there are no complex technologies for processing these waste, which would ensure environmental safety and economic benefit during their large-scale processing.

Following current trends and predetermining the prospects, in our opinion, the separation of valuable compounds from ash and slag, including rare metals, trace elements, aluminosilicate microspheres and other components, is of particular interest. However, an assessment of the directions of the integrated use of ash and slag waste is possible only after studying the composition of their mineral part, which is the task of this study.

Methods. As objects of research were used ash and slag waste (ASW) of thermal power plant (TPP-1) in Pavlodar, which are products of high-temperature (1200–1700 ° C) processing of the mineral, non-combustible part of the coal. The ash particle size is less than 1 mm.

X-ray fluorescence analysis was performed on an X-Ray Innov-X Systems instrument. The chemical composition of the ash was investigated by X-ray phase analysis on an automated DRON-3 diffractometer with $Cu_{K\alpha}$ - radiation.

Ash processing in an alkaline medium is carried out (alkali concentration 100, 200, 300 and 400 g / l) in a heat-resistant glass with a capacity of 250 ml. The caustic soda solution is preliminarily thermostated to the required temperature, after which ash is introduced with constant stirring. The exposure time was from 1 to 4 hours. The leaching temperature was 55, 70, 80 and 90 ° C.

The method of photometric determination of aluminum with aluminone [8], based on the ability of the Al^{3+} ion to form a red sparingly soluble complex compound with aluminum. The reaction is carried out at pH=4.9 in the presence of ammonium sulfate. Optical density is measured at 540 nm. The sensitivity of the method is 0.05 mg / l aluminum. Iron oxide (Fe^{3+}) can interfere with the analysis. The influence of iron with a mass concentration of 0.3 mg / l and more is eliminated by its reduction with ascorbic acid to ferrous iron (Fe^{2+}).

Photometric determination of iron with sulfosalicylic acid [9]: 10 ml of the analyzed water is poured into a 50 ml conical flask. This volume should contain from 1 to 10 μg of iron, which corresponds to concentrations from 0.1 to 1 mg / l. Wastewater more concentrated in terms of iron content is pre-diluted in a volumetric flask so that the iron content in 10 ml of the resulting solution is within the specified limits. Then 5 ml of sulfosalicylic acid solution and 5 ml of ammonia solution are poured into the test tube.

Results and its discussion. The results of studies of X-ray fluorescence and X-ray gas analyzes are shown in tables 1 and 2.

Table 1. **Content of metals in ASW**

Element	Content, %
Si	40.06
Fe	5.90
Al	14.31
Ni	1.36
Cu	0.48
Zn	1.44
Ca	3.96
Pb	1.34
Na	0.26
Mg	0.74
Cd	1.38
K	1.11
Sn	1.28
Ti	1.91
Other	24.47

Analysis of table 1 indicates a high content of metals in the composition of ash and slag waste. The main component of ash and slag waste at TPP-1 is silicon. It is also worth noting that the class of mineral impurities in the studied ash and slag waste can be attributed to sorption with an increased content of metals Ca, Al, Mg, Fe (total content about 25%). The total alkali metal content is 1.37%.

Table 2. **Content of components in ASW**

Component	Content, %
SiO_2	54,5
TiO_2	0,75
Al_2O_3	19,4
Fe_2O_3	6,6
MnO	0,14
MgO	1,64
CaO	4,3
Na_2O	0,34
K_2O	1,56
SO_3	0,14
P_2O_5	0,24
Other	10,39

In terms of chemical composition, the basis of these ash and slag waste (about 80%) are oxides of silicon, aluminum and iron (Table 2). The increased content of SiO_2 and Al_2O_3 in the ash indicates the presence of aluminosilicate microspheres, the main trace elements of which are sillimanite $Al_2O_3 \times SiO_2$ or mullite $3Al_2O_3 \times 2SiO_2$ [10].

Considering the fact that ash and slag waste is a promising mineral resource base of valuable metals, and the removal of harmful metals such as Al, Fe, Ti, Cd, Pb, is of great importance for the destruction of waste in the environment.

To extract metals of basic and amphoteric character from ash and slag waste, the method of leaching with solutions of mineral acids (H_2SO_4, HCl, HNO_3) is used. The authors of [11] note that toxic metals can be strongly leached under acidic conditions, since acid treatment affects the chemical characteristics of the slag and, thus, affects the structure of heavy metals.

Various alkaline solutions (NaOH, Na_2CO_3, $NaHCO_3$, NH_4OH) are used to extract trace elements of an acidic and amphoteric nature. In view of the increased content of silicon oxides in the ash sample, the alkaline leaching method was chosen. In this work, studies were carried out to determine the optimal conditions (temperature, alkali concentration and duration of the process) for leaching a sample of the ash and slag waste under study.

The results of studying the effect of temperature on the degree of extraction of aluminum and iron were carried out according to the procedures [8, 9]. The data obtained are shown in Table 3.

Table 3.**Impact of temperature on the degree of extraction of aluminum and iron**

Temperature, °C	Fe		Al	
	m, g	a, %	m, g	a, %
55	0,66±0,02	36,8	0,78±0,05	17,7
70	0,85±0,03	57,2	0,89±0,06	20,2
80	1,28±0,04	71,1	1,03±0,05	23,3
90	1,29±0,04	71,5	1,04±0,05	23,5

From the results of Table 3, it was revealed that the temperature has a significant effect on the extraction of iron: with an increase in temperature from 70 to 80 ° C, an increase in yield of 13.9% is noted, however, a further increase in temperature to 90 ° C does not lead to noticeable changes.

For the extraction of aluminum, a similar situation is observed, but with lower rates. Therefore, at a temperature of 80 ° C, the Al yield was only 23.3%, at 90 ° C - 23.5%. As a result of the tests carried out, it was found that the optimum temperature for leaching is 80 ° C.

The results of determining the influence of alkali concentration on the degree of extraction of aluminum and iron are presented in the form of a dependence diagram (Figure 1).

Figure 1 shows that with an increase in the concentration of alkali from 100 to 200 g / l, there is a significant increase in the degree of extraction of both aluminum (by 6.6%) and iron (by 34.9%). A further increase in the alkali concentration to 300 g / l leads to a decrease in the degree of metal recovery.

Data on the study of the effect of leaching time on the degree of extraction of aluminum and iron are shown in Table 4.

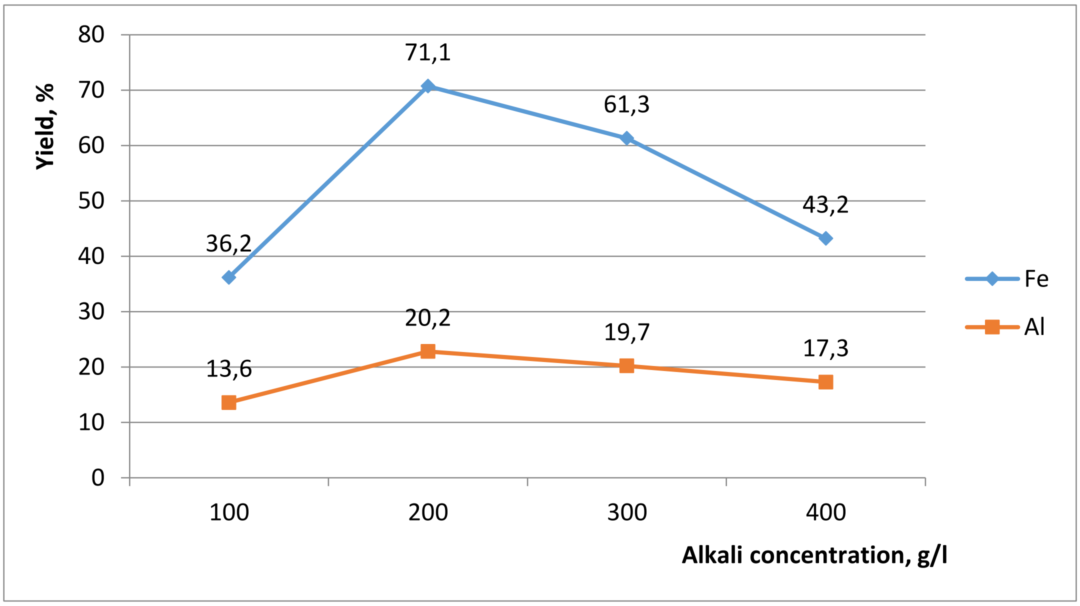

Fig. 1. Dependence of the degree of extraction of aluminum and iron on the concentration of alkali

Table 4. Dependence of the degree of extraction of aluminum and iron on time

Leaching time, h	Iron recovery, %	Aluminum recovery, %
1	49,8	19,6
2	71,1	23,3
3	74,1	32,2
4	79,3	46,9

As can be seen from Table 4, the dependence is linear with increasing reaction time, the yield of metals increases. It is important to note that for the extraction of aluminum, there is a positive trend with an increase in the contact time up to 4 hours.

Based on the value of the aluminum metal, it was decided to conduct research until it is completely extracted from ash waste by repeated treatment with an alkali solution. In order to accelerate the process of aluminum leaching, desilicated ash was successively treated with fresh alkali solutions in 3 stages for one hour. The data of the studies carried out are shown in Table 5.

Table 5. **Completeness of extraction of aluminum with repeated treatment with alkali solutions**

Stage	Time of processing, h	a_{Al}, %
I (desiliconization)	3	32,2
II	1	46,7
III	1	64,1
IV	1	78,2

The results of table 5 indicate that multiple processing of desilicated ash leads to the maximum extraction of aluminum (up to 78%).

Therefore, it can be concluded that the leaching time and alkali concentration have the greatest influence on the degree of extraction of aluminum, the temperature is less, and the degree of extraction of iron is greatly influenced by the concentration, and the lowest temperature and time.

Another promising direction in the processing of ash and slag waste is their use as fillers in the construction industry. The need for partial replacement is currently explained by the increasing demand for fillers and aggregates in the construction of road surfaces. Research in this direction continues.

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КҮЛ-ҚОЖ ҚАЛДЫҚТАРЫН ҚАЙТА ӨҢДЕУ

Аңдатпа. Бұл мақала Павлодар қаласындағы 1-ЖЭО-да пайда болатын жылу электр станцияларының күл-қожды қалдықтарын кәдеге жаратудың перспективалық бағыттарын анықтауға арналған. Күл-қож қалдықтарының құрамы оларды одан әрі пайдаланудың ең қолайлы аймағын анықтау мақсатында рентгенофлуоресценттік және рентгенофазалық талдау әдістерімен қаралды. Алынған мәліметтерге сүйене отырып, қалдықтарды алюминий және темір сияқты қымбат металдарды сілтілі шаймалау арқылы алу үшін пайдалану ұсынылды. Жұмыста металды шаймалаудың ең оңтайлы жағдайларын (температура, сілтінің концентрациясы, процестің ұзақтығы) таңдау нәтижелері көрсетілген. Темірді алу үшін оңтайлы жағдайлар 80 °С температурада 3-4 сағат бойы концентрациясы 200 г/л каустикалық натриймен сілтілі ортада күл-қож қалдықтарын өңдеу

болып табылады. Алюминийді алу дәрежесін арттыру үшін күл-қож қалдықтарын сілтінің жаңа ерітінділерімен бір сағат ішінде 3 кезеңде дәйекті өңдеуден тұратын сілті ерітіндісімен қайта өңдеуді қолдану қажет..

Негізгі сөздер: өнеркәсіптік қалдықтар, күл-қож қалдықтары, металдар, шаймалау, кәдеге жарату.

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ПЕРЕРАБОТКА ЗОЛОШЛАКОВЫХ ОТХОДОВ

Аннотация. Данная статья посвящена выявлению перспективных направлений утилизации золошлаковых отходов тепловых электростанций, а именно отходов, образующихся на ТЭЦ-1 в г. Павлодаре. Рассмотрен состав золошлаковых отходов методами рентгенофлуоресцентного и рентгенофазового анализа с целью выявления наиболее подходящей области их дальнейшего использования. На основании полученных данных было предложено использовать отходы для извлечения драгоценных металлов, таких как алюминий и железо, путем щелочного выщелачивания. В работе представлены результаты подбора наиболее оптимальных условий (температура, концентрация щелочи, продолжительность процесса) выщелачивания металлов. Установлено, что оптимальными условиями для извлечения железа является обработка золошлаковых отходов в щелочной среде едким натром концентрацией 200 г/л при температуре 80 °C в течение 3-4 часов. Для повышения степени извлечения алюминия необходимо применять повторную обработку раствором щелочи, заключающуюся в последовательной обработке золошлаковых отходов свежими растворами щелочи в 3 этапа в течение одного часа.

Ключевые слова: промышленные отходы, золошлаковые отходы, металлы, выщелачивание, утилизация.