

Thermodynamic Evaluation of Possibility of Fluoride Processing of Some Types of Technogenic Raw Material

*Hamdamov Dilshod Xaydarovich*¹, *Kamolov Tursunboy Ochilovich*²,
*Borbat Vladimir Fyodorovich*³

Annotation: The work presents a thermodynamic assessment of the possibility of fluoride processing of some types of technogenic raw materials.

Key words: slag, cake, energy, clinker, extract, pulp.

The necessity of ash and slag waste fluorine recycling was shown. The possibility of ashe and slag waste recycling with hydrofluoric acid was stying. Our experiments and thermodynamics calculate show the perspective ness of the usage of hydrofluoric acid as extract agent. It will provide the high degree of utilization of ash and slag waste and the receipt of wide spectrum of products for various fields of industry.

In some industrial wastes from chemical, metallurgical, and energy enterprises, the main macrocomponents are oxides of silicon, aluminum, and iron. Such types of waste include tailings, slag, dust, clinker, saline solutions, slurries of metallurgical production, ash and slag waste (ASW), solid fuel products of thermal power plants, etc., which currently even do not process or partially process them.

The work [1–5] provides an overview of the technologies for processing this type of technogenic raw materials, however, the absence of an integrated technology for their processing with the extraction of valuable components that meet the requirements of economic, environmental, and technological feasibility does not allow large-scale utilization.

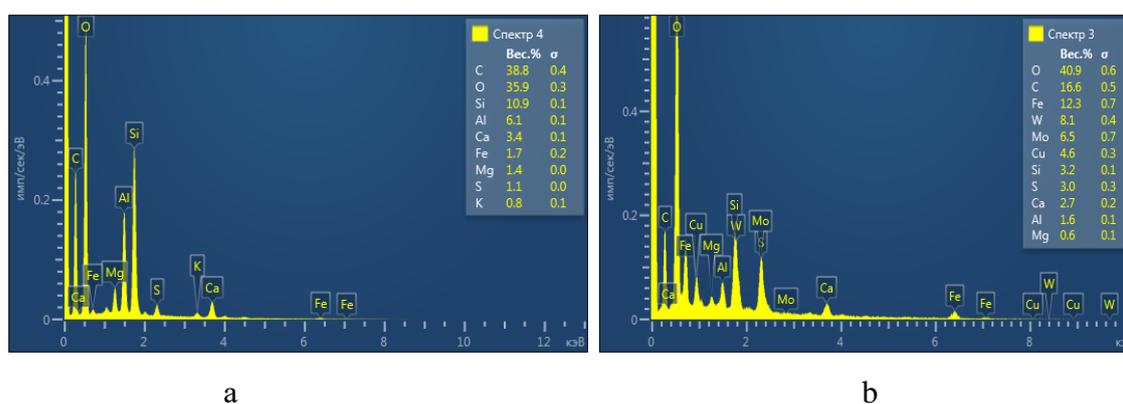


Figure 1. Energy dispersive spectra of ASW (a) and Mo-cake (b)

The most acceptable is, at the initial stage, the separation of macrocomponents of silicon oxides, aluminum and iron at which enrichment occurs in terms of the content of valuable metals.

Fig. 1 shows the energy dispersion spectra of ASW of the Novoangrenskaya TPP and cakes of molybdenum production of the NPO "Rare metals and hard alloys" of JSC "Almalyk MMC".

¹Karshi engineering-economics institute, Karshi

²SUE "Fan va Tarakkiyot" at TSTU named after Karimov I.A., Tashkent

³Omsk State University named after Dostoevsky V.F. Omsk



As can be seen from fig. 1, the content of macrocomponents (weight, %) Si-3.2-10.9; Fe-12.3-1.7; Al-1.6-6.1, respectively, in the cake and ASW. The main minerals included in the waste according to the XRD data are: quartz (SiO_2), muscovite, mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), $(\text{KAl}_{2.20}(\text{Si}_3\text{Al})_{0.975}\text{O}_{10}(\text{OH})_{1.72-0.28})$, diopside ($\text{Ca}(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$), hematite (Fe_2O_3), magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), microcline ($\text{K}_{0.92}\text{Na}_{0.08}\text{Al}_{0.99}\text{Si}_{3.01}\text{O}_8$), aluminum phosphate ($\text{Al}(\text{PO}_4)$). The presence of mullite in the ASW [2,6] makes ineffective the use of traditional methods of processing aluminosilicate materials due to its high resistance to chemical attack.

Based on the composition of the ASW, it can be assumed that the use of fluoride technology [8] will avoid these difficulties due to the high reactivity of fluorine-containing agents and to obtain a number of valuable products. A preliminary thermodynamic analysis of the fluoride processing process allows us to determine the most possible products. We calculated the thermodynamic characteristics of ongoing processes.

Based on the chemical composition of the ASW, the leaching reactions of silicon and aluminum when treated with hydrofluoric acid solutions proceed as follows:

1. $\text{SiO}_2(\text{s}) + 4\text{HF}_{(\text{aq})} = \text{SiF}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta G = -12,1 \text{ kJ/mol}$
2. $\text{SiF}_4(\text{g}) + 2/3\text{H}_2\text{O}(\text{l}) = 1/3\text{SiO}_2(\text{s}) + 2/3\text{H}_2\text{SiF}_6(\text{aq}); \Delta G = -20,9 \text{ J/mol}$
3. $\text{Al}_2\text{O}_3(\text{s}) + 6\text{HF}_{(\text{aq})} = 2\text{AlF}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l}); \Delta G = -217,9 \text{ kJ/mol}$
4. $2\text{AlF}_3(\text{s}) + 6\text{HF}_{(\text{aq})} = 2[\text{AlF}_6]^{3-} + 6\text{H}^+_{(\text{aq})}; \Delta G = 5,0 \text{ kJ/mol}$

The values of isobaric-isothermal potentials show that the formation of aluminum and silicon fluoride complexes is likely due to their high thermodynamic stability. And the formation of iron fluoride complexes does not occur under standard conditions, which is shown by the Gibbs energy of the formation reactions.

5. $\text{Fe}_2\text{O}_3(\text{s}) + 6\text{HF}_{(\text{aq})} = 2\text{FeF}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l}); \Delta G = -88,7 \text{ kJ/mol}$
6. $2\text{FeF}_3(\text{s}) + 6\text{HF}_{(\text{aq})} = 2[\text{FeF}_6]^{3-} + 6\text{H}^+_{(\text{aq})}; \Delta G = 33,1 \text{ kJ/mol}$

This is apparently due to the low stability of the iron fluoride complex in dilute solutions of hydrofluoric acid [9].

Aluminum can form two types of $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ and AlF_3 compounds with hydrofluoric acid, of which the formation of $\text{AlF}_3\cdot 3\text{H}_2\text{O}$, which does not dissolve in hydrofluoric acid, is thermodynamically more likely. However, with increasing temperature, the Gibbs energy of the reaction for the formation of $\text{AlF}_3\cdot 3\text{H}_2\text{O}$ increases, therefore, the reaction is thermodynamically more likely to proceed along the following steps:

7. $3\text{Al}_2\text{O}_3(\text{s}) + 6\text{HF}_{(\text{aq})} + 3\text{H}_2\text{O}(\text{l}) = \text{AlF}_3\cdot 3\text{H}_2\text{O}(\text{s}); \Delta G = -48,1 \text{ kJ/mol}$
8. $2\text{AlF}_3\cdot 3\text{H}_2\text{O}(\text{s}) + 6\text{HF}_{(\text{aq})} = 2[\text{AlF}_6]^{3-}_{(\text{aq})} + 6\text{H}^+_{(\text{aq})} + 6\text{H}_2\text{O}(\text{l}); \Delta G = -164,8 \text{ kJ/mol}$

Based on the data of x-ray phase analysis, the presence of a mullite phase in the ASW determines a different reaction:

9. $3\text{Al}_2\text{O}_3 + 2\text{SiO}_2(\text{s}) + 48\text{HF}_{(\text{aq})} = 6[\text{AlF}_6]^{3-}_{(\text{aq})} + 2\text{H}_2\text{SiF}_6(\text{ag}) + 18\text{H}^+ + 13\text{H}_2\text{O}(\text{l});$
 $\Delta G = -722,2 \text{ kJ/mol}$

When mullite is dissolved, fluoride complexes of aluminum and silicon are formed, and a high value of the Gibbs energy of the reaction indicates a spontaneous process.

Table 1. Gibbs energy of the reactions of the formation of micronutrient fluorides

Ongoing reaction	ΔG , kJ/mol
$\text{BaO}(\text{s}) + 2\text{HF}_{(\text{aq})} = \text{BaF}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$	-315,73
$\text{La}_2\text{O}_3(\text{s}) + 6\text{HF}_{(\text{aq})} = 2\text{LaF}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l})$	-751,63
$\text{SrO}(\text{s}) + 2\text{HF}_{(\text{aq})} = \text{SrF}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$	-295,41



$ThO_2 (s) + 4HF_{(aq)} = ThF_4 (s) + 2H_2O (l)$	-125,13
$MgO(s) + 2HF_{(aq)} = MgF_2 (s) + H_2O (l)$	-175,63
$Ga_2O_3(s) + 6HF_{(aq)} = 2GaF_3 (s) + 3H_2O (l)$	-98,96
$ZrO_2 (s) + 4HF_{(aq)} = ZrF_4 (s) + 2H_2O (l)$	-129,68
$CuO (s) + 2HF_{(aq)} = CuF_2 (s) + H_2O (l)$	-67,46
$Na_2O (s) + 2HF_{(aq)} = 2NaF (s) + H_2O (l)$	-453,93
$K_2O(s) + 2HF_{(aq)} = 2KF(s) + H_2O(l)$	-441,56
$2MnO_2(s) + 4HF_{(aq)} = 2MnF_2 (s) + O_2 (g) + 2H_2O (l)$	-81,56
$CaO (s) + 2HF_{(aq)} = CaF_2(s) + H_2O(l)$	-253,52

Other elements present in the ASW during the interaction with hydrofluoric acid solutions form mostly insoluble fluorides, which is proved by the performed thermodynamic calculations (Tab. 1).

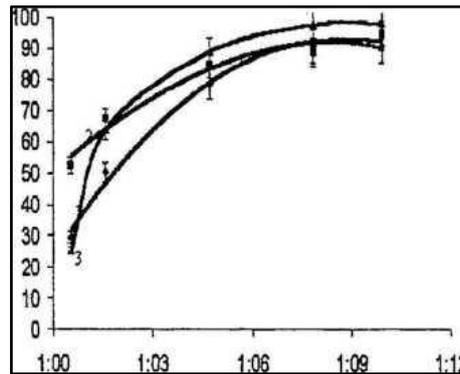


Figure 2. Dependence of the degree of extraction of macrocomponents on the S:L ratio: for Al - 1, for Fe - 2, for Si - 3

High negative values of Gibbs energy obtained in thermodynamic calculations indicate the spontaneous course of the process of leaching of aluminum, silicon and iron when treated with solutions of hydrofluoric acid.

In this process, it is also possible to concentrate rare and rare earth elements in the resulting sludge. Thus, the performed thermodynamic calculations show the effectiveness of using hydrofluoric acid as a leaching agent.

An experimental study of the basic laws of leaching of aluminum, silicon, and iron was carried out in a thermostatically controlled polypropylene cell with mechanical stirring. The analysis was carried out according to [9, 10, 11].

It was experimentally established that when treated with a concentrated solution of hydrofluoric acid with an increase in the ratio of solid and liquid phases from 1:2 to 1:8, the degree of extraction increases, which is apparently associated with a gradual decrease in pulp viscosity. The results are shown in tab. 2 and in fig. 2.

Table 2. The dependence of the degree of extraction of macrocomponents on the S:L ratio during treatment with concentrated hydrofluoric acid, mp (weight) = 10 g

S:L	1:1	1:2	1:5	1:8	1:10
$\alpha_{Al}, \%$	29,5	50,3	78,6	91,0	91,0
$\alpha_{Fe}, \%$	52,5	67,4	84,7	88,9	94,4
$\alpha_{Si}, \%$	25,4	64,0	89,1	98,0	98,5



Fig. 3 shows the dependence of the degree of extraction of macrocomponents on the concentration of HF solution.

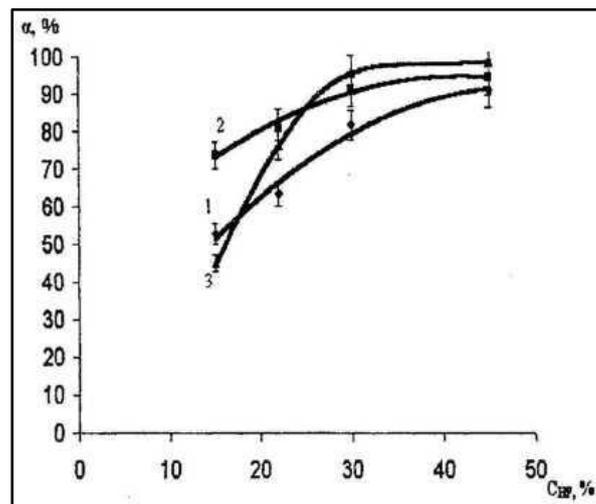


Figure 3. Dependence of the degree of extraction of macrocomponents on the concentration of HF solution: 1 for Al, 2 for Fe, 3 for Si.

As can be seen from Fig. 3, the effect of the concentration of hydrofluoric acid was studied in the range from 15 to 45% with the ratio T: W = 1:10. It was found that the highest degree of extraction is provided by concentrated hydrofluoric acid (45%) (Table 4).

Table 3. Extraction of macrocomponents from ASW at various processing times; T: W = 1:10, t (hitch) = 10 g

Mass loss, %	t, min.						
	1	2	5	10	30	60	120
In a 45% solution	21	56	85	84	85	84	84
In a 30% solution	10	27	54	54	53	54	54

In the table. 3 shows the data of the dependence of the weight loss of the ASW sample on the processing time at a ratio of S:L 1:10. From the table. Figure 3 shows that the process is characterized by a high initial extraction rate. The main part of the macrocomponents is extracted from the ASW in 5-10 minutes, after which the processing time of up to 2 hours practically does not affect the degree of extraction.

The effect of the concentration of hydrofluoric acid was studied in the range from 15 to 45% | with the S:L ratio = 1:10. It was found that the highest degree of extraction provides concentrated hydrofluoric acid | (45%) (table. 4).

Table 4. The effect of the concentration of hydrofluoric acid on the degree of extraction of aluminum and iron at S:L = 1:10, t (sample) = 10 g

Degree of extraction, %	Acid concentration, $C_{HF} \%$			
	45	30	22	15
$\alpha_{Al}, \%$	91,0	81,7	63,4	52,9
$\alpha_{Fe}, \%$	94,4	91,3	81,8	73,7
$\alpha_{Si}, \%$	98,5	98,2	76,3	45,1

It can be seen from the above data that, when the ASW is treated with hydrofluoric acid solutions, aluminum, silicon, and iron are converted into a solution with a fairly high degree of recovery.

Thus, confirmation of thermodynamic calculations by experimental data shows the promise of using fluoride ASW processing. This will provide a high degree of extraction of macrocomponents and



obtain a wide range of products for various industries. Further, deeper thermodynamic analysis and experimental study of the fluoride ASW processing process will allow predicting the reaction mechanisms taking into account the dispersion of the ASW, as well as providing process optimization and the construction of a kinetic and thermodynamic leaching model.

Bibliography

1. Borbat V.F., Mikhailov Yu.L., Adeeva L.N. Kompleksnaya pererabotka zoli-unosa ekibastuznogo uglya kak novogo istochnika sirya redkix, redkozemelnix metallov [Complex processing of fly ash and slag waste from Ekibastuz coal as a new source of raw materials for rare, rare-earth metals] // *Thes. doc. Int. scientific conf. "Metallurgiya XXI veka - shag v budushcheye"* ["*Metallurgy of the 21st century is a step into the future.*"] Krasnoyarsk, 1998. p. 204.
2. Sharipov Kh.T., Borbat V.F., Kamolov T.O., Adeeva L.N., Tupesebekov A.Kh. Mineralogo-geokhimicheskiye osobennosti zoloshlakovykh otkhodov TES i ikh utilizatsiya s vydeleniyem makro- i mikrokomponentov. [Mineralogical and geochemical features of ash and slag waste from thermal power plants and their utilization with the extraction of macro- and microcomponents]. Tashkent.: "Muharrir" 2012. p. 208
3. Borbat V.F., Mikhailov Yu.L., Adeeva L.N. and others. Issledovaniye vozmozhnosti obogashcheniya zoly- unosa TETS po redkim i tsvetnym metallam dlya ikh posleduyushchego izvlecheniya [Investigation of the possibility of enrichment of fly ash and slag waste from thermal power plants for rare and non-ferrous metals for their subsequent extraction] // *Khimiya i khimicheskaya tekhnologiya* [Chemistry and Chemical Technology]. 1999.V. 42. Issue. 5. pp. 86-90.
4. Borbat V.F., Mikhailov Yu.L., Golovanova O.A. Termodinamicheskoye prognozirovaniye form nakhozhdeniya mikroelementov v zole ekibastuzskikh ugley [Thermodynamic forecasting of the forms of trace elements in the ash of Ekibastuz coals] // *Vestnik Omskogo universiteta*. [Tomsk State University Journal]. 2000. Issue. 2. p. 42-44.
5. Guzhelev EP, Usmansky KT. Ratsional'noye primeneniye zoly TETS: Rezul'taty nauchno-prakticheskikh issledovaniy [Rational use of ash from thermal power plants: Results of scientific and practical research]. Omsk: Omsk. gos. un- t, [Omsk: Omsk. state un.], 1998. p. 238.
6. Liner Yu.A. Kompleksnaya pererabotka alyuminiysoderzhashchego syr'ya kislotnymi sposobami [Complex processing of aluminum-containing raw materials by acid methods]. M.: Nauka, 1982. p. 208.
7. Nurkeev S. S. Zoloshlaki ekibastuzskikh ugley - perspektivnoye syr'ye dlya proizvodstva sul'fata alyuminiya [Ash and slag waste of Ekibastuz coal - a promising raw material for the production of aluminum sulfate] // *Tr. Ural, nauch.-issled. khim. in-ta* [Tr. Ural, Chemical research institute], 1988. No. 65. pp. 81-84.
8. Ishikawa N. Ftor: khimiya i primeneniye [Fluorine: chemistry and application]. M.: Mir, 1982.
9. Kiseleva E.K. Analiz ftorsoderzhashchikh soyedineniy [Analysis of fluorine-containing compounds]. M .; L .: Chemistry, 1966. p. 219.
10. Myshlyaeva L.V., Krasnoshchekov V.V. Analiticheskaya khimiya kremniya [Analytical chemistry of silicon]. M .: Nauka [Science], 1972. p. 210.
11. Tikhonov V.N. Analiticheskaya khimiya kremniya [Analytical chemistry of silicon]. M.: Nauka [Science], 1971. p. 266.

