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

Kamolov T.O.,Sharipov Kh.T., Borbat V.F., Akhmedova F.S., Bozorov A.N.

SUE "Fan va taraqqiyot" Tashkent state technical university named after Islam Karimov, Tashkent, Uzbekistan
SUE "Fan va taraqqiyot" Tashkent state technical university named after Islam Karimov, Tashkent, Uzbekistan
Omsk State University named after Dostoevsky V.F., Omsk, Russia
SUE "Fan va taraqqiyot" Tashkent state technical university named after Islam Karimov, Tashkent, Uzbekistan
SUE "Fan va taraqqiyot" Tashkent state technical university named after Islam Karimov, Tashkent, Uzbekistan

ABSTRACT: The necessity of ash and slag waste **fluorine** recycling was **shown.** The possibility of ashe and slag waste recycling with hydrofluoric acid was styding. 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 recept of wide spectrum of products for various fields of industry.

KEY WORDS: **macrocomponent**, thermodynamic, technogenic raw material, **clinker**, silicon oxide, muscovite, mullite, aluminum phosphate, hydrofluoric acid, experiment planning.

I. INTRODUCTION

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.

II. RESULTS OF THE INVESTIGATIONS AND DISCUSSION

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.
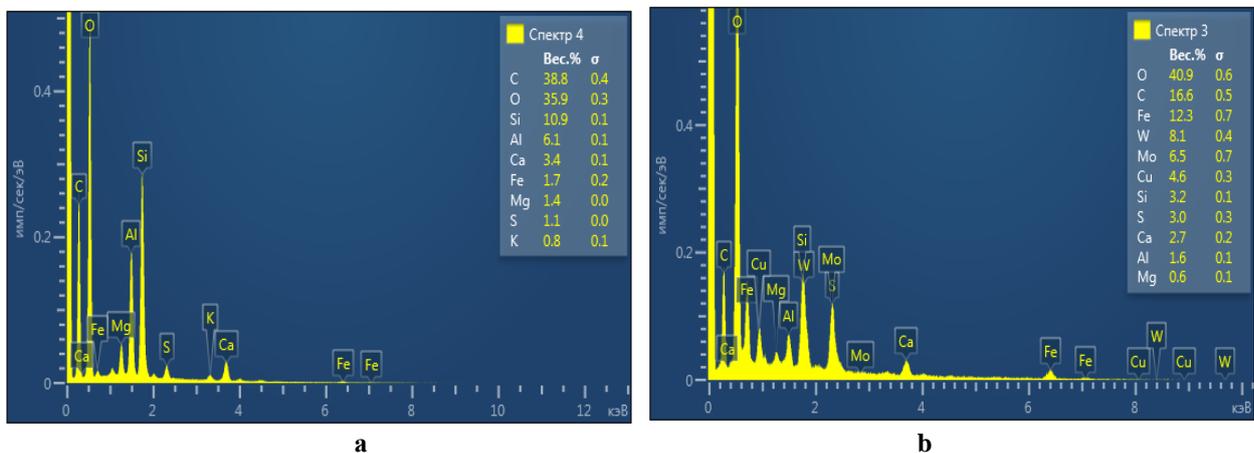

a   b
Figure 1. Energy dispersive spectra of ASW (a) and Mo-cake (b)

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 Novo-Angren TPP and cakes of molybdenum production of the RPU "Rare metals and hard alloys" of JSC "Almalyk MMC".

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 ($Al_6Si_2O_{13}$), ($KAl_{2.20}(Si_3\ Al\ )_{0.975}O_{10}(OH)_{1.720.28}$), diopside ($Ca(Mg,\ Fe,\ Al)\ (Si,\ Al)_2O_6$), hematite ($Fe_2O_3$), magnetite ($FeO \cdot Fe_2O_3$) microcline ($K_{0.92}Na_{0.08}Al_{0.99}Si_{3.01}O_8$), aluminum phosphate ($Al\ (PO_4)$). 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. SiO_2 (s) $+4HF_{(aq)}$ =SiF_4(g) $+2H_2O$ (l); ΔG = -12,1 kJ/mol
2. SiF_4 (g) $+2/3H_2O$ (l) = $I/3SiO_2$**(s)**$+2/3H_2SiF_{6(aq)}$; ΔG =-20,9 J/mol
3. Al_2O_3(s)$+6HF_{(aq)}$ = $2AlF_3$(s)$+3H_2O$ (L); ΔG =-217,9kJ/mol
4. $2AlF_3$(s) $+6HF_{(aq)}$ = $2[AlF_3]^{3-}$) + $6H+_{(aq)}$; ΔG =5,0 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. Fe_2O_3(s)$+6HF_{(ag)}$ = $2FeF_3$ (s)$+3H_2O$ (l); ΔG =-88,7 kJ/mol
6. $2FeF_3$(s) $+6HF_{(ag)}$ = $2[FeF_6]^{3-}$ $+6H^+_{(aq)}$; ΔG =33,1 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 $Al_2O_3.3H_2O$ and AlF_3 compounds with hydrofluoric acid, of which the formation of AlF_3 $3H_2O$, 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 AlF_3 $3H_2O$ increases, therefore, the reaction is thermodynamically more likely to proceed along the following steps:

7. $3Al_2O_3$(s)$+6HF_{(aq)}$$+3H_2O$(l) = $AlF_3 \cdot 3H_2O$(s); ΔG =- 48,1 kJ/mol
8. *$2AlF_3 \cdot 3H_2O$(s)$+6HF_{(aq)}$=$2[AlF_6]^{3-}_{(aq)}$$+6H^+_{(aq)}$$+6H_2O$(l); Δ G = - 164,8 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. *$3Al_2O_3$ $2SiO_2$(s)$+48HF_{(aq)}$=$6[AlF_6]^{3-}_{(aq)}$$+2H_2SiF_{6(ag)}$$+18H^+$$+13H_2O$(l)*; ΔG = - 722,2 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
$BaO(s)+2HF_{(aq)}$ =BaF_2(s)$+H_2O$(l)	-315,73
La_2O_3(s)$+6HF_{(ag)}$= $2LaF_3$(s)$+3H_2O$ (l)	-751,63
$SrO(s)+2HF_{(aq)}$=SrF_2(s)$+H_2O$ (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)$+6HF_{(ag)}$ =$2GaF_3$ (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

$2MnO_2(s)+4HF_{(aq)}= \quad 2MnF_2 \quad (s)+O_2$ $(g)+2H_2O$ (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).
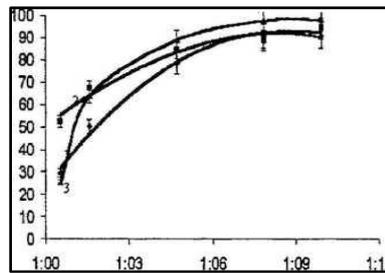

Figure 2. Dependence of the degree of extraction of macrocomponents on the S:L ratio: forAl -1, for Fe-2, for Si-3

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
α_{Al}, %	29,5	50,3	78,6	91,0	91,0
α_{Fe}, %	52,5	67,4	84,7.	88,9	94,4
α_{Si}, %	25,4	64,0	89,1	98,0	98,5

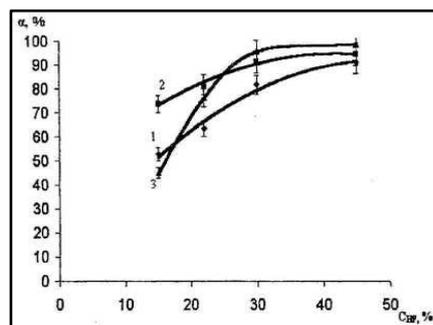Fig. 3 shows the dependence of the degree of extraction of macrocomponents on the concentration of HF solution.

Figure 3. Dependence of the degree of extraction of macrocomponents on the concentration of HF solution: 1 for A1,2 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	2	5	8	84	85	84	84
In a 30% solution	1	2	5	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 f 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
α_{Al}, %	91,0	81,7	63,4	52,9
α_{Fe}, %	94,4	91,3	81,8	73,7
α_{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.

III. CONCLUSION

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.

REFERENCES

1. Sharipov Kh.T., Kamolov T.O., Borbat V.F. Utilization of ash and slag waste from thermal power plants with the release of micro- and macrocomponents. Ed. "Muharrir", Tashkent-2012, 208 p
2. Borbat V.F., Mikhailov Yu.L., Adeeva L.N. Complex processing of fly ash from Ekibastuz coal as a new source of raw materials for rare, rare-earth metals. Tez. report int. scientific. conf. "Metallurgy of the XXI century - a step into the future". Krasnoyarsk, 1998. p. 204.
3. Borbat V.F., Mikhailov Yu.L., Adeeva L.N. et al. Investigation of the possibility of enrichment of fly ash from thermal power plants for rare and non-ferrous metals for their subsequent extraction. Chemistry and chemical technology. 1999. T. 42. Issue. 5. p. 86-90.
4. Borbat V.F., Mikhailov Yu.L., Golovanova O.A. Thermodynamic Prediction of Forms of Trace Element Locations in Ash of Ekibastuz Coals. Vestn. Ohm. un-that. 2000. Issue. 2. p. 42-44.
5. Guzhelev E.P., Usmansky K.T. Rational use of ash from thermal power plants: Results of scientific and practical research. Omsk: Omsk state un-t, 1998. p. 238.
6. Liner Yu.A. Complex processing of aluminum-containing raw materials by acid methods. Moscow: Nauka, 1982.p. 208.
7. Nurkeev S.S. Ash and slag from Ekibastuz coals - a promising raw material for the production of aluminum sulfate. Tr. Ural, scientific research. chem. inst., 1988. No. 65. p. 81-84.
8. Isikawa N. Fluorine: chemistry and application. Moscow: Mir, 1982.
9. Kiseleva E.K. Analysis of fluorine-containing compounds. M .; L .: Chemistry, 1966.p. 219.
10. Myshlyaeva L.V., Krasnoshchekov V.V. Analytical chemistry of silicon. Moscow: Nauka, 1972.p. 210.
11. Tikhonov V.N. Analytical chemistry of silicon. Moscow: Nauka, 1971, p. 266.