

SEPARATION OF SILICON-IRON-COPPER-NICKEL CONCENTRATE BY FLUORAMMONIUM METHOD INTO INDIVIDUAL OXIDES

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Processes of ammonium hydrodifluoride interaction with main components of copper-nickel concentrates – iron, copper, nickel oxides have been investigated. Thermodynamics of chemical reactions was calculated. Thermogravimetric analyses were carried out. The main kinetic parameters – activation energy and interaction rate constant of ammonium hydrodifluoride with iron, copper, nickel oxides were experimentally determined. Manufacturing sequence allowing us to separate individual oxides from oxide mixture was proposed.

Introduction

Processing copper-nickel ores the necessity of removing iron and silicon oxides from the bulk of ore mass occurs. Methods of hydrofluoride recycling may be an alternative to the existing methods of their removal [1]. The possibility of processing raw material with concentrated solution of hydrofluoric acid was concerned [2], but practically it is more reasonable to use ammonium fluoride for opening silicate materials. After opening silicate constituent of mineral raw material with fluorides further segregation of valued components by classic hydrometallurgical methods is possible. The advantage of using ammonium fluoride as an open agent is a possibility of its regeneration.

The method is based on the difference of fluoride properties of raw material constituents. Some fluorides are volatile and easily separated from the bulk. Other fluorides are soluble. Some of them undergo pyrohydrolysis or have different pH precipitation. As fluoride mixture is obtained in ammonium fluoride melt after fluoridation then it is possible to select modes for complete separation of mineral mixture per individual components varying the differences in physicochemical properties of fluorides [3].

The main type of raw materials for obtaining copper is sulfide ores, in sulfide copper-nickel ores the main minerals are pentlandite, millerite, chalcopyrite, cubanite, pyrrhotine, magnetite. Ammonium fluorides interaction with silicon oxide is studied rather detailed [4], therefore, it is not considered in the given paper. Within the bounds of the given work the possibility of separation of silicon, iron, copper and nickel oxides from ore concentrate by fluoride ammonium method was studied.

1. Thermodynamic analysis and thermogravimetric investigations

The results of thermodynamic calculations of oxide fluoridation reactions are given in Table 1, equilibrium of chemical reactions was determined by the method of Temkin-Schwartzmann subject to the fact that substance heat capacity does not depend on temperature [4].

It was determined that fluoridation of copper oxide with ammonium hydrofluoride is possible higher than 420 K, of nickel oxide – higher than 315 K, iron oxide – higher than 310 K.

Table 1. Temperature dependence of enthalpy and Gibbs energy of hydrofluoridation reaction of metal oxides with ammonium hydrofluoride, kJ/mole

Reaction	Index	298, K	400, K	600, K
$\text{CuO} + \text{NH}_4\text{F} \cdot \text{HF} = \text{CuF}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$	ΔH	86	74	52
	ΔG	32	4	-43
$\text{NiO} + \text{NH}_4\text{F} \cdot \text{HF} = \text{NiF}_2 + \text{NH}_3 + \text{H}_2\text{O}$	ΔH	59	47	24
	ΔG	4,8	-24	-72
$\text{Fe}_2\text{O}_3 + 3\text{NH}_4\text{F} \cdot \text{HF} = 2\text{FeF}_3 + 3\text{H}_2\text{O} + 3\text{NH}_3$	ΔH	177	142	74
	ΔG	8	-79	-225

Thermogravimetric and differential thermal analyses of interaction of copper, nickel and iron oxides with ammonium hydrofluoride were carried out. The experiments were carried out at matched TGA/DSK/DTA analyzer – derivatograph of the type SDT Q600 with software data processing TA instruments Universal V4.2E. Sample mass is up to 25 mg, sensitivity of balance is 0,1 mcg. Calorimetric accuracy/reproducibility is $\pm 2\%$ (by metal standard). DTA sensitivity is 0,001 °C. Thermocouples are Pt/Pt-Rh (type R). Crucibles: platinum.

Due to the high heating rate the shift of heat flow peaks relative to mass loss occurs and in this connection the derivative of heat flow by time was used for defining accurate location of process change by mass.

The diagrams of copper oxide (II) interaction with ammonium hydrofluoride are given in Fig 1.

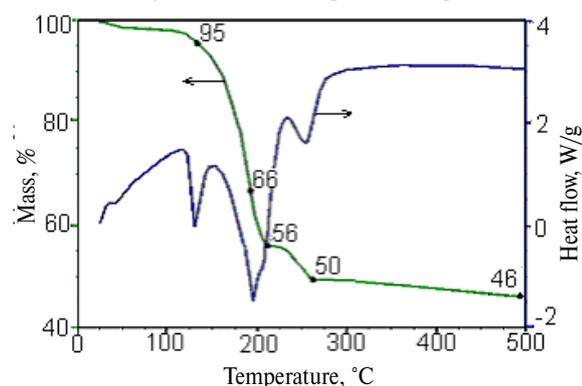
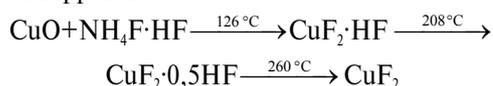


Fig. 1. Thermogravimetric and differential thermal analyses of copper oxide (II) interaction with ammonium hydrofluoride

It follows from Fig. 1 that melting temperature of ammonium hydrofluoride amounts to 126 °C then the process of copper oxide hydrofluoridation occurs, and excess ammonium hydrofluoride is sublimated with de-

composition at 240 °C. The formation of system $\text{CuF}_2 \cdot x\text{HF}$ occurs at melting temperature of ammonium hydrofluoride. At 208 °C $\text{CuF}_2 \cdot 0,5\text{HF}$ is formed. At 260 °C complex fluoride is damaged and CuF_2 is formed. Then hydrolysis of copper fluoride with water air vapors occurs. The reaction courses with heat release.

On the basis of thermogravimetric investigations the following chemical transformation chain courses at ammonium hydrofluoride interaction with copper oxide may be supposed.



Thermograms of nickel oxide (II) interaction with ammonium hydrofluoride are given in Fig. 2.

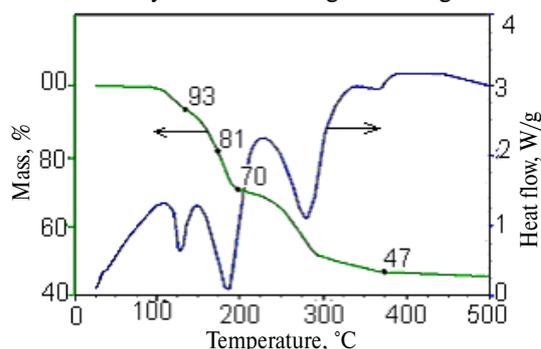


Fig. 2. Thermogravimetric and differential thermal analyses of nickel oxide (II) interaction with ammonium hydrofluoride

It follows from Fig. 2 that melting temperature of ammonium hydrofluoride amounts to 126 °C then the process of nickel oxide hydrofluoridation courses; excess ammonium hydrofluoride is sublimated with decomposition. At melting temperature of ammonium fluoride the complex $(\text{NH}_4)_2\text{NiF}_4$ is formed. At 195 °C – the original complex is decomposed to NH_4NiF_3 . At 372 °C – NiF_2 is formed. Reaction courses with heat release.

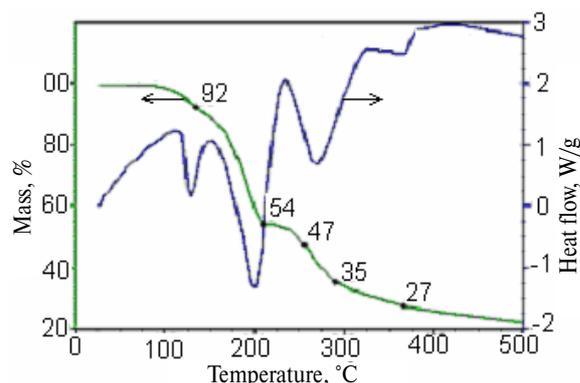
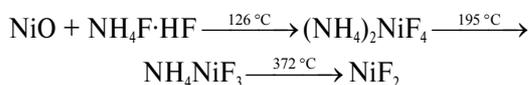


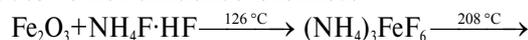
Fig. 3. Thermogravimetric and differential thermal analyses of iron oxide (III) interaction with ammonium hydrofluoride

Ammonium hydrofluoride interaction with nickel oxide and successive thermal decomposition of complex fluorides may be described by the following chemical transformation chain.



Thermograms of iron oxide (III) interaction with ammonium hydrofluoride are given in Fig. 3.

It follows from Fig. 3 that at melting temperature of ammonium hydrofluoride the complex fluoride $(\text{NH}_4)_3\text{FeF}_6$, is formed which is damaged up to $(\text{NH}_4)_2\text{FeF}_5$ at 255 °C, and at 290 °C – up to NH_4FeF_4 . At 365 °C iron trifluoride is formed.



Then the process of iron fluoride hydrolysis with water air vapors courses. Reaction courses with heat release.

2. Kinetic researches

Laboratory device, shown in Fig. 4, was assembled for studying kinetic parameters of hydrofluoridation of copper, nickel, iron oxides with ammonium hydrofluoride.

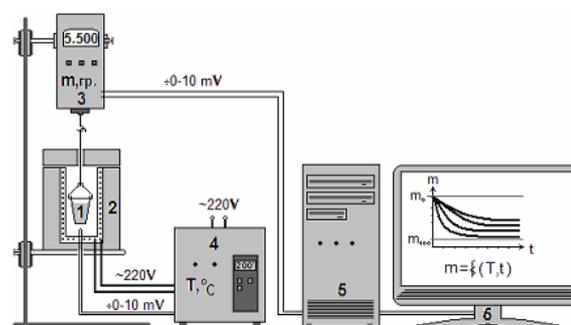


Fig. 4. Laboratory device: 1) platinum crucible with a batch, 2) heating furnace, 3) balance, 4) microprocessor system regulator «Termoluks», 5) module of balance signal processing, 6) monitor

Batch which was suspended to the balance and placed into the furnace with preset temperature was put into crucible. Kinetic characteristics of interaction of metal different oxides with ammonium hydrofluoride were defined by mass diminution. The results of the experiment are given in Fig. 5.

The dependence of conversion degree on time is described by the following equation for copper oxide; substituting the desired temperature and time in the given equation it is possible to calculate the response degree of the initial substance into the product at the desired conditions:

$$\alpha = 1 - [1 - (1100 \cdot \exp(-78000/RT) \cdot \tau)^{1/2}]^3$$

Activation energy of the process amounted to 78 kJ/mole. The process courses in kinetic response area. The way of process acceleration is temperature increase.

Kinetics of nickel oxide hydrofluoridation with ammonium hydrofluoride was similarly studied, Fig. 6.

The dependence of conversion degree on time for nickel oxide is given in Fig. 6 and described by the following equation:

$$\alpha = 1 - [1 - (2 \cdot 10^6 \cdot \exp(-102000/RT) \cdot \tau)^{1/2}]^3$$

Activation energy of the process amounted to 102 kJ/mole. The process courses in kinetic response area. The method of process acceleration is temperature increase.

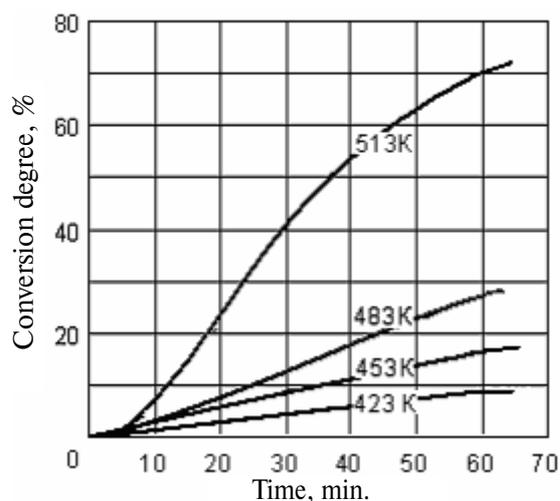


Fig. 5. Dependence of response degree on time for the process of copper oxide hydrofluoridation with ammonium hydrofluoride at different temperatures

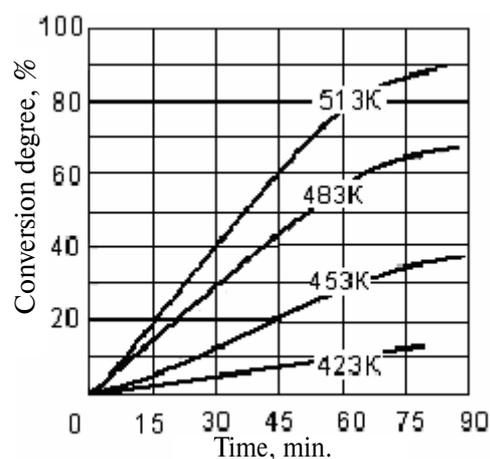


Fig. 6. Dependence of response degree on time for the process of nickel oxide hydrofluoridation with ammonium hydrofluoride at different temperatures

For iron oxide (III) the dependence of conversion degree on time is given in Fig. 7 and described by the following equation:

$$\alpha = 1 - [1 - (470 \cdot \exp(-66500/RT) \cdot \tau)^{1/2}]^3.$$

Activation energy of the process amounted to 66,5 kJ/mole. The process courses in kinetic response area. The method of process acceleration is temperature increase.

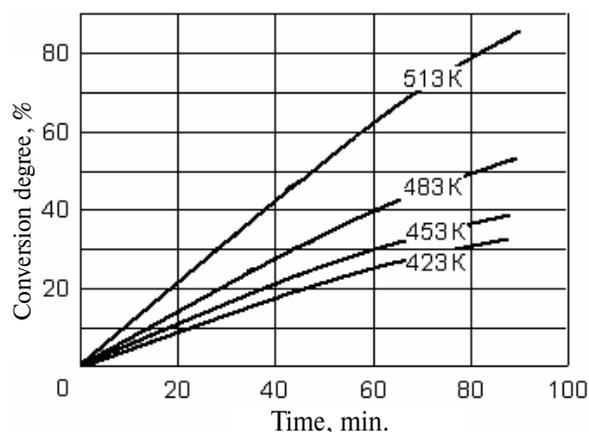


Fig. 7. Dependence of response degree on time for the process of iron oxide (III) hydrofluoridation with ammonium hydrofluoride at different temperatures

3. Process flowsheet

On the basis of carried out investigations of interaction processes of copper, iron and nickel oxides with ammonium hydrofluoride the process flowsheet of separation process of ore concentrate on individual oxides was developed (Fig. 8). The only agent used for the given process is ammonium fluoride (NH_4F) or ammonium hydrofluoride ($\text{NH}_4\text{F} \cdot \text{HF}$) which is reclaimed and returns to the head of the process for decomposition of new raw material set. Ammonium fluoride is reclaimed when it is influenced by ammonia water at any fluorides.

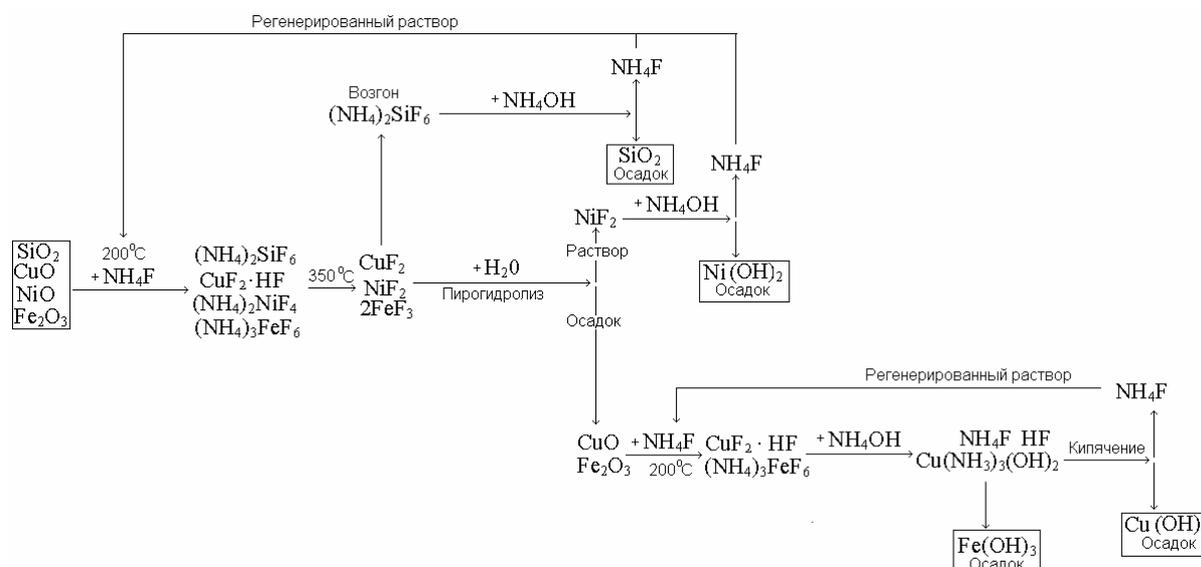


Fig. 8. Process flowsheet of separation of mineral oxide mixture of silicon, iron, copper and nickel into individual oxides

Pyrohydrolysis process of copper and iron fluorides are described in scientific literature [6]. The behavior of copper ammine is described in scientific literature [7].

At fluoridation of silicon-iron-copper-nickel concentrate with ammonium fluorides the complex fluoride compounds of silicon $(\text{NH}_4)_2\text{SiF}_6$, copper $\text{CuF}_2 \cdot \text{HF}$, nickel $(\text{NH}_4)_2\text{NiF}_4$ and iron $(\text{NH}_4)_3\text{FeF}_6$ are formed. When heating fluoridated mixture at temperature 20...350 °C, ammonium hexafluorosilicate $(\text{NH}_4)_2\text{SiF}_6$ is evaporated as a result the original mixture is desilicized. The rest copper, nickel and iron fluorides are treated with water vapor at temperature 100...150 °C. In this case nickel fluoride does not react with water vapor and copper and iron fluorides underwent pyrohydrolysis and change into oxide form. When the obtained mixture is treated with water nickel fluoride remains in solution (solubility of NiF_2 is 26 g/l), and iron and copper oxides precipitate. The released iron and copper oxides are treated again with ammonium fluorides for obtaining complex fluorides. The mixture of iron and copper fluorides is treated with ammonia water. As a result of the reaction ferric hydroxide precipitates and copper fluoride changes into the form of soluble ammonia.

Thus, the assigned aim is achieved – silicon-iron-copper-nickel concentrate is separated into individual oxides.

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Conclusions

1. It was shown by thermodynamic calculations that hydrofluoridation reaction of iron, copper, and nickel oxides with ammonium hydrofluorides is possible at temperatures higher than 420 K.
2. Using thermogravimetric technique it was shown that copper, nickel, iron fluorides formation at their oxides interaction with ammonium fluoride courses through the stages of formation of fluoride ammonium complexes which are successively decomposed.
3. Dependence of conversion degree on time for the process of oxides hydrofluoridation in temperature range 423...513 K is described by the following equation:
for CuO: $\alpha=1-[1-(1100 \cdot \exp(-78000/RT) \cdot \tau)^{1/2}]^3$;
for NiO: $\alpha=1-[1-(2 \cdot 10^6 \cdot \exp(-102000/RT) \cdot \tau)^{1/2}]^3$;
for Fe_2O_3 : $\alpha=1-[1-(470 \cdot \exp(-66500/RT) \cdot \tau)^{1/2}]^3$.
4. Technological sequence of fluoride ammonium cycle for processing copper-nickel concentrate with extraction of copper and nickel oxides into separate fractions was suggested. The main point of the technique is in processing oxide mixture with ammonium fluoride at further separation of fluorides, reclaiming and returning ammonium fluoride to the cycle.

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