



Research on Obtaining Gadolinium Oxide from Waste Technologies for Processing of Uranium-gadolinium Containing Materials

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Abstract: One of the activities of the Uranium production of JSC "UMP" is the processing of hard-to-open uranium-gadolinium-containing scraps. When processing materials of this type, after their dissolution, the gadolinium fluoride precipitation operation is carried out with the subsequent extraction purification of the obtained uranyl nitrate solutions. At the deposition stage, almost all the gadolinium contained in the scraps is transferred to the GdF_3 precipitate and sent to the tailings dump as part of the solid waste. In order to determine the possibility of obtaining gadolinium oxide from waste processing of uranium-gadolinium containing materials, exploratory studies were initiated. In the course of the work, various methods of obtaining gadolinium oxide were tested. A number of experiments were carried out to refine the modes of obtaining gadolinium oxide by the method of two-stage precipitation of oxalate. A technological scheme was developed, according to which a finished product was obtained, suitable for further use in the technology of obtaining uranium-gadolinium tablets of UMP JSC. The scheme consists of the following main operations: dissolution of gadolinium fluoride in a solution of aluminum nitrate, precipitation of gadolinium oxalate, washing of gadolinium oxalate in the first stage of precipitation with a solution of nitric acid, conversion of oxalate to gadolinium hydroxide, dissolution of hydroxide in a solution of nitric acid, re-precipitation of gadolinium oxalate, calcination to gadolinium oxide.

Keywords: Rare Earth Elements, Precipitation of Oxalates, Gadolinium Oxide

1. Introduction

Gadolinium fluoride contains other rare earth elements (samarium, europium, terbium, yttrium, etc.).

Due to the extreme proximity of the properties of REE, separating them and obtaining compounds of individual elements is one of the most difficult tasks of chemical technology. Currently, all REES without exception have been obtained with a high degree of purity. Such successes in the separation of REE have been achieved thanks to the use of modern separation methods - ion exchange and extraction [1]. However, until now, many enterprises producing REE use, along with new and old, so-called classical separation methods - fractional crystallization, fractional deposition, methods using a change in valence. Classical methods are

less effective, but due to their simplicity and the use of non-deficient and cheap reagents, they retain their significance at the initial stages of separation, where separate concentrates are obtained, from which compounds of individual REES of high purity are isolated by extraction and ion exchange methods [2].

In the fractional (fractional) crystallization method, it is proposed to use many different compounds. However, many of them, due to their low efficiency and the use of expensive reagents in some cases, have lost their practical significance [3].

In comparison with fractional crystallization, fractional precipitation gives a higher enrichment coefficient, although the deposition itself is more complicated, because it is necessary to filter and rinse. The main disadvantage of the

method, which reduces the efficiency of separation, is the formation of local supersaturation at the time of addition of the precipitator. To prevent such phenomena, various methods are resorted to: buffer mixtures are introduced, additives selectively increasing solubility. Recently, the method of "homogeneous" deposition has become quite widespread, in which the precipitator is formed in the solution itself [4].

The most widespread is the precipitation of REE in the form of hydroxides. The method is based on the difference in the pH of precipitation of hydroxides, which increases from Lu to La in connection with an increase in the main properties in this direction. The pH of the precipitation of REE depends on the medium from which the precipitation is carried out; this is due to the fact that, along with the hydroxides, basic REE salts are formed [5].

A common disadvantage of the fractional hydroxide deposition method is the need to work with very dilute solutions. In addition, the process is greatly complicated in some cases by poor filterability and high absorption capacity of precipitation.

In the production of rare earth elements, the ability of REE to form double sulfates and oxalates is of great interest from the point of view of separating the impurities present. These properties of rare earths have been widely used in the development of technology for the production of gadolinium oxide of nuclear purity from gadolinium-containing materials [6].

As part of this work, an analysis of existing methods for obtaining gadolinium from industrial waste was carried out.

A known method for extracting gadolinium from waste from the production of storage devices (gadolinium-gallium garnets), developed by E. Gusset (US Patent 4 198231, April 15, 1980; Swiss Aluminum Ltd., Switzerland), is designed to isolate gallium and gadolinium from waste containing both of these elements in the form of oxides or compounds converted into oxides.

The waste is finely ground and then dissolved in strong mineral acids. Gadolinium is precipitated from purified solutions in the form of oxalate, gallium is released in metallic form electrolytically [7].

The disadvantage of this method is that to convert gadolinium into a soluble form, an expensive and highly aggressive reagent is used with respect to metals – hydrochloric acid.

A patent is known under the authorship of: Polyakova L. A. (RU), Nikitina E. V. (RU), Monastireva Y. A. (RU), Pryakhina P. I. (RU), Pashina O. V. (RU), Zaitseva V. V. (RU) "Method for obtaining gadolinium oxide".

The organic mixture is dissolved in hydrochloric acid at a ratio of S:L=1: 1.8, the process temperature is 80-90°C for 4 hours. Next, gadolinium oxalate is precipitated. The ratio of the mass of oxalic acid to the mass of the organic mixture is 1.3:1. The precipitated powder is filtered, washed, dried at a temperature of 170-180°C for 4.5-5 hours and calcined at a temperature of 870-900°C [8].

However, the disadvantage of this method of obtaining

gadolinium oxide is an unsatisfactory percentage of the final product yield.

2. The Experimental Part

The most suitable methods, in relation to the technology existing in the uranium production of JSC "UMP", are the methods of precipitation and extraction. The separation of REE can be carried out in the form of hydroxides or basic salts [9]. Since uranium co-precipitation occurs during the production of hydroxide, methods of precipitation of double sulfates or oxalates were chosen for the separation of gadolinium, since gadolinium forms double salts with alkali metal salts that are practically insoluble in excess of sulfate, and oxalates with oxalic acid.

At the first stage of the research, experiments were carried out to select a method for converting gadolinium into a solution. It is known from these sources of scientific and technical information [10] that rare earth element fluorides (REE) do not dissolve in water, cold and hot dilute acids. REE fluoride precipitates can be converted into a soluble form by treating with a solution of aluminum nitrate. A solution of aluminum nitrate was used as a solvent precipitate of GdF_3 agent. During the experiments, the ratio of solid and liquid phases, the concentration of aluminum and nitric acid were varied.

The diagram of the dependence of the degree of dissolution of gadolinium on the ratio of solid and liquid phases S:L and the concentration of aluminum in the solvent agent is shown in Figure 1.

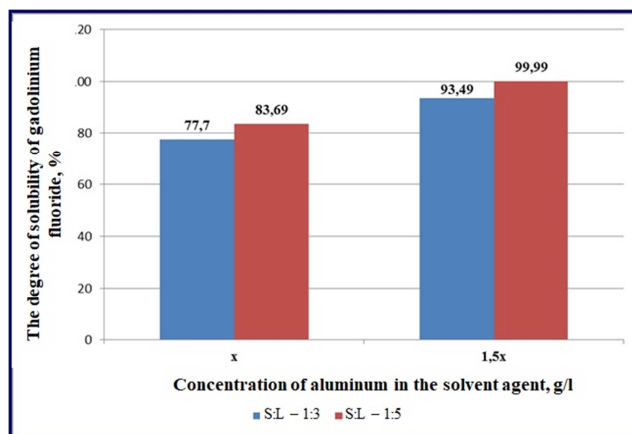


Figure 1. Diagram of the dependence of the degree of dissolution of gadolinium in solution on the ratio of S:L and the concentration of aluminum.

The analysis of the experimental results showed that with an increase in the ratio of the S:L phases and the concentration of aluminum, the degree of dissolution of gadolinium increases from 77,75 to 99,99%. With an increase in the concentration of HNO_3 , the degree of dissolution of gadolinium decreases from 83,69% to 22,09%.

In the course of the research, experiments were performed to obtain gadolinium oxide by sulfate deposition. The separation of double sulfates was carried out from a solution containing gadolinium 63,0 g/l, uranium 1,3 g/l, nitric acid

18,7 g/l. Precipitation $\text{Na}_3[\text{Gd}(\text{SO}_4)_3]$ was dissolved in nitric acid with repeated precipitation of double sulfate. The resulting precipitate was calcined to gadolinium oxide. The gadolinium content in the final oxide (figure 2) was 40,66%, which is 46,87% of the theoretical content. The low degree of gadolinium extraction and the unsatisfactory nuclear purity of the oxides obtained in this case – 40,66% for gadolinium-forced the abandonment of the scheme for obtaining gadolinium oxide through intermediate precipitation of double sulfates and initiated the search for other methods.

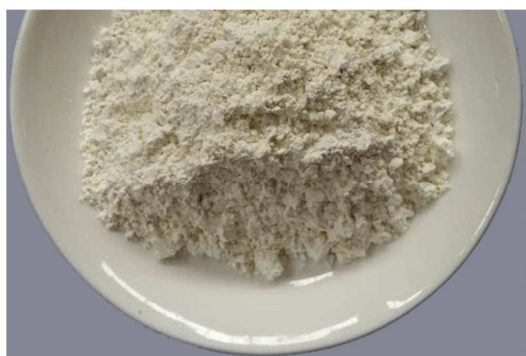


Figure 2. Image of gadolinium oxide obtained by sulfate deposition.

It is known from sources of scientific and technical information that the method of oxalate deposition is widely used in the production of rare earth elements, which allows almost completely getting rid of the main impurities: iron, aluminum, calcium and others. When using multi-stage deposition of oxalates, it is possible to obtain REE of almost nuclear purity [11].

Gadolinium oxalate was isolated from solutions obtained after dissolving the GdF_3 precipitate in aluminum nitrate. The content of gadolinium in the solution was 63,8 g/l, uranium 1,5 g/l. During the experiments, the concentration of nitric acid and the flow rate of the precipitating agent were varied.

Based on the results of the experiments, a diagram of the dependence of the degree of gadolinium deposition on the consumption of oxalic acid and the residual concentration of nitric acid in solution was constructed (Figure 3).

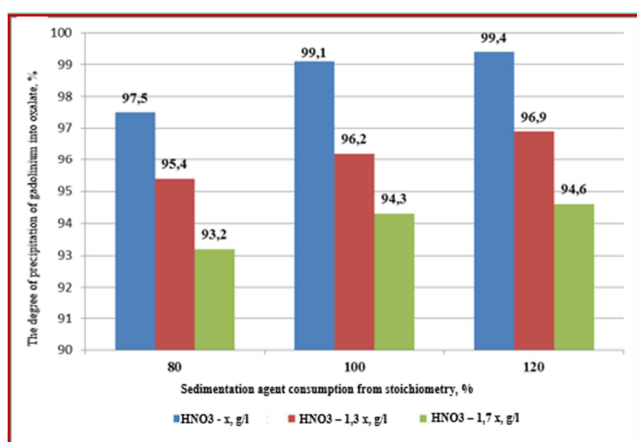


Figure 3. Diagram of the dependence of the degree of gadolinium deposition on the consumption of oxalic acid and the residual concentration of nitric acid in solution.

Based on the results of the performed experiments, it was concluded that with an increase in the consumption of $\text{H}_2\text{C}_2\text{O}_4$, the degree of precipitation of Gd increases slightly, at the same time, an increase in the residual acidity of the solution leads to a decrease in the degree of precipitation.

The gadolinium oxalate precipitate was calcined and the gadolinium content in the resulting oxide was measured. The gadolinium content was at the level of 70,45%, which is 81,20% of the theoretical content.

According to the literature data, multi-stage purification is required to obtain gadolinium compounds of nuclear purity: the oxalate of the first deposition is dissolved in nitric acid and the oxalate of the next stage is precipitated from the resulting solution, the degree of purity of the final product is mainly determined by the number of purification stages.

In order to increase the degree of gadolinium extraction, experiments were carried out according to the scheme of two-stage precipitation of gadolinium oxalate.

Gadolinium oxalate, according to NTI sources, has an extremely low solubility in neutral and acidic environments. For example, in 2N nitric acid, the solubility of gadolinium oxalates is 2,7 g/l. Gadolinium hydroxide has a high degree of dissolution [12]. Therefore, before dissolving in nitric acid, gadolinium oxalate of the first stage of precipitation was converted to the form $\text{Gd}(\text{OH})_3$. During the experiments, different conditions for conducting the process were tested.

Based on the experimental results, graphs of the dependence of the degree of gadolinium extraction into the solution on the reagent consumption on stoichiometry and the duration of the process were constructed (Figure 4). With an increase in these indicators, the extraction of gadolinium into the solution increases from 62,83 to 83,55%.

To select the optimal mode of dissolution of gadolinium hydroxide in nitric acid, the concentration of HNO_3 was varied during the experiments. According to the data obtained during the experiment, a diagram of the dependence of the degree of gadolinium extraction into solution on the concentration of nitric acid in the solvent agent was constructed, shown in Figure 5.

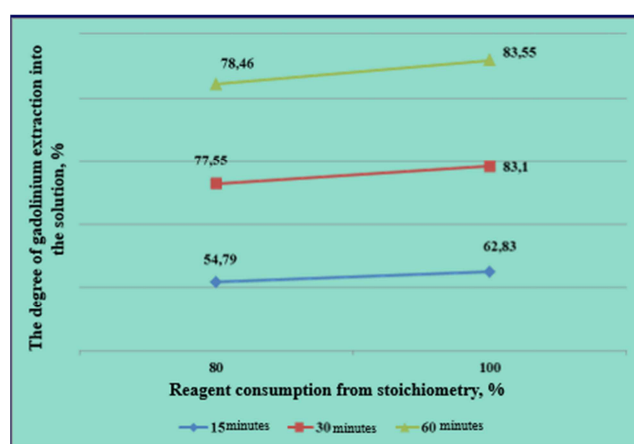


Figure 4. Graphs of the dependence of the degree of gadolinium extraction into the solution on the reagent consumption on stoichiometry and the duration of the process.

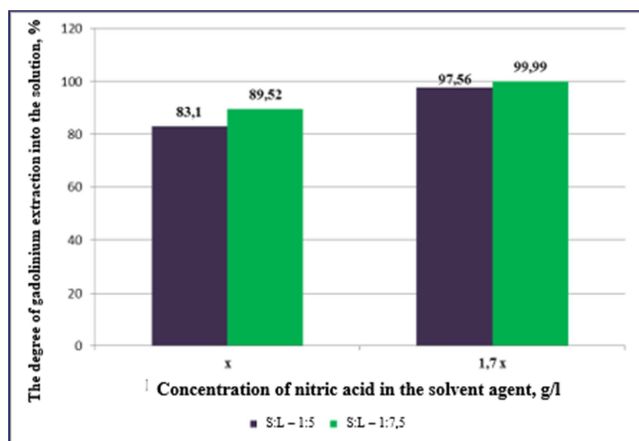


Figure 5. Diagram of the dependence of the degree of gadolinium extraction into solution on the concentration of nitric acid in the solvent agent.

Based on the experimental results, it can be concluded that with an increase in the concentration of nitric acid in the solvent agent, the extraction of gadolinium into the solution increases from 89,52 to 99,99%.

The processes of precipitation and calcination of gadolinium oxalate were carried out in previously established modes. The gadolinium content in the resulting gadolinium oxide was at the level of ~ 81,57%, which is 94,02% of the theoretical content.

At the next stage of research, experiments were performed to study the effect of precipitation conditions for a more complete extraction of gadolinium into oxalate. One of the main factors that have a significant impact on the composition of the sediment obtained as a result of precipitation is the time of its maturation [13].

Studies on the effect of maturation time were carried out on gadolinium oxalate precipitates obtained after repeated precipitation from solutions with a residual concentration of nitric acid 444,0 g/l, gadolinium – 38,44 g/l, uranium – 0,086 g/l. The sediment exposure in solution varied from 1 to 24 hours. Then the precipitate was subjected to high-temperature treatment and analytical control of the gadolinium content in the final oxide was carried out.

Based on the results of the experiments performed, it can be concluded that with an increase in the maturation time of gadolinium oxalate from 1 to 8 hours, the gadolinium content in the oxide increases from 81,57% to 82,25%. A further increase in the sediment maturation time leads to a slight increase in the gadolinium content in the oxide.

The method of rapid cooling of the solution after holding oxalate for 1, 4 and 8 hours was also tested. Cooling was carried out by loading a glass with a solution and a precipitator into a larger chemical beaker filled with tap water with a temperature of + 15°C. The use of the method of rapid cooling of the solution after the introduction of oxalic acid made it possible to reduce the holding time of the gadolinium oxalate precipitate and obtain a product with a gadolinium content of 82,28%.

To assess the suitability of the obtained gadolinium oxide, it was added to uranium nitrous oxide in an amount of 8.0% by weight.

The results of the analytical determination of the content

of chemical impurities indicate that the uranium nitrous oxide powders obtained during the experiment with the introduction of gadolinium oxide do not meet the requirements of the technical specification for the total content of aluminum, calcium, magnesium and silicon.

To assess the possibility of obtaining gadolinium oxide, which provides the required nuclear purity of uranium nitrous oxide powders, two-stage precipitation experiments were conducted with intermediate washing of gadolinium oxalate in the first stage of deposition.

It is known from sources of scientific and technical information that oxalates of lead, cadmium, bismuth, copper, aluminum and trivalent iron are easily dissolved in 0,1–0,5 N acid solutions. Oxalates of zinc, nickel, and divalent iron are completely dissolved in 1N nitric acid [14].

During the experiments, the gadolinium oxalate precipitate of the first stage of precipitation was washed with nitric acid solutions. The ratio of the S:L phases was 1:5, the time was 30 minutes. Then gadolinium oxalate was washed with alkali, gadolinium hydroxide was dissolved in a nitric acid solution. Further, gadolinium oxalate was isolated by precipitation, followed by its rolling. The gadolinium content in gadolinium oxide was 85,86%.

In order to determine the possibility of using the obtained reagent in the production technology of uranium-gadolinium fuel, gadolinium oxide was mixed with uranium nitrous oxide in an amount of 8%. The results of the analytical determination of the content of chemical impurities indicate that the powders of uranium nitrous oxide with the introduction of gadolinium oxide obtained according to the scheme of two-stage precipitation with acid treatment of gadolinium oxalate of the first stage of deposition meet the requirements of the technical specification.

At the next stage of research, it is planned to analyze scientific and technical information in the field of methods for reducing the level of radioactivity of rare earth elements. It is also planned to conduct laboratory studies on the possibility of reducing the radioactivity of gadolinium oxide obtained earlier.

3. Conclusion

- 1) Based on the results of the research, a technological scheme for obtaining gadolinium oxide by two-stage precipitation of gadolinium oxalate with intermediate washing of the oxalate of the first stage of precipitation with a solution of nitric acid has been developed.
- 2) The developed technology opens up the prospect of obtaining a product that will later be used in the technology of producing uranium-gadolinium tablets in the uranium production of JSC "UMP". The presented technology is economically profitable, since its implementation does not require the purchase of new equipment and the creation of new production facilities.
- 3) The implementation of the technology for obtaining gadolinium oxide from gadolinium fluoride-waste from uranium production makes it possible to reduce the volume of solid radioactive waste of JSC"UMP", which in turn will contribute to improving the radiation

situation in the area of the enterprise's tailings storage facility.

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