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PLASMA CONVERSION OF VOLATILE FLUORIDES AND NITRIC ACID SOLUTIONS

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ABSTRACT

High-quality oxide materials have a sweeping application in various fields of the modern nuclear industry. As an example the role of uranium in nuclear power is well known. We suggest here a practically universal method for the synthesis of numerous metal oxides (above all, uranium oxide) and mixed oxide compositions, based upon an efficient plasma decomposition of a sprayed metal solution.

Nitrate solution is dispersed by a nebulizer into the plasma-air stream. The solution drops mix with plasma and convert to oxides of dissolved metals, water vapor, nitrogen oxides, nitrogen and oxygen.

Major elements of the developed flow sheet are: a plasma generator (a plasma torch and a power source), a plasma chamber (converter), and a particulate air filter (PAF).

The plasma chamber is the heart of the plasma set for manufacturing a finely dispersed uranium oxide from the nitrate solution. Fast and homogeneous mixing of the feed solution with the plasma stream is provided by a conic form of the liquid flow injected into the plasma torch; the solution drops penetrating the plasma stream are decelerated or accelerated.

Solid and gaseous phases are separated in the PAF. The resulting powdery materials must be brought out of the reaction zone, preventing, or efficiently slowing down all subsidiary recombination processes.

The filter off-gas is then directed into a condenser, where water vapor is condensed and nitrogen oxides are partly absorbed. The condensate is used for the total absorption of nitrogen oxides. The offered method allows to obtain practically all metal oxides of unique physical and chemical properties from appropriate nitrate solutions.

INTRODUCTION

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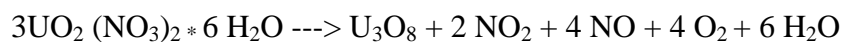
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Nitrate solutions and melts are basic products of the hydrometallurgical processing in nuclear industry. The principal scheme of industrial production of metal oxides includes the following stages: precipitation of metal salts, filtration, drying, calcination, reprocessing (or dumping) of the raffinate, sorption of the off-gas (nitrogen oxides). The plasmachemical approach to production of metal oxides is based upon the disintegration of a source metal solution by its injection into the plasma reactor, where the dispersed solution sharply boils up to dryness followed by instant high temperature heating and formation of metal oxides and off-gases (water vapor, nitrogen oxides and oxygen).

Plasmachemical decomposition of the $\text{UO}_2(\text{NO}_3)_2$ - solution is generally described by the overall reaction:



The principal scheme of the process is shown in Fig. 1.

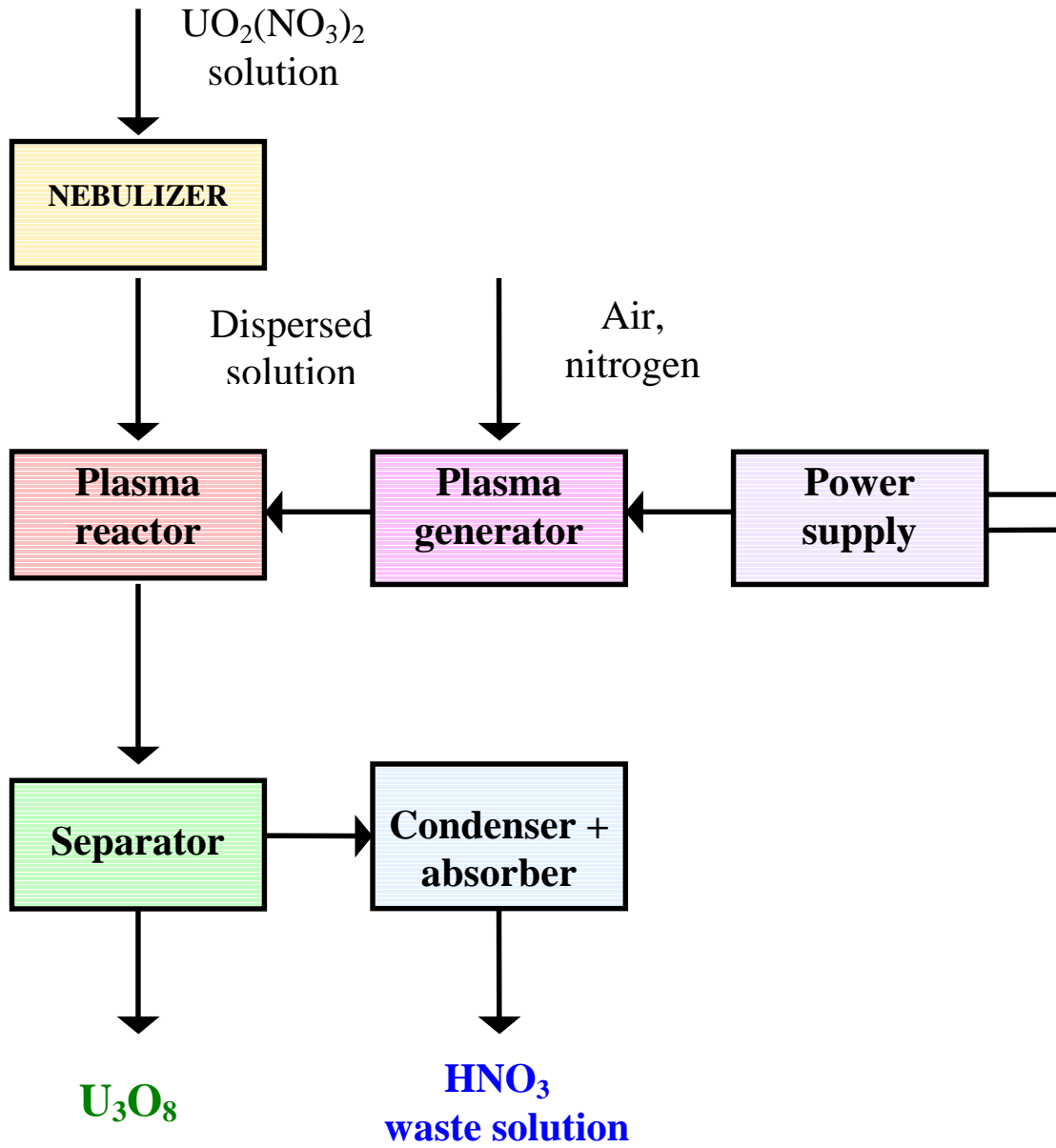


Figure 1. Principal diagram of fine metal oxide production by decomposition of nitric acid solutions in plasma torch.

The complex flow sheet scheme compiles the following units:

1. Power supply for plasma torch.
2. Plasma torch, where gaseous stream forms the low-temperature plasma. To reprocess the nitric acid solution -see equation (I)- it is possible to use an air, nitrogen or oxygen. Taking economic parameters into account, the air plasma is the most expedient option. The additional advance of this method is the low nitrogen oxides formation rate.
3. Plasma reactor, where the source solution is mixed with plasma and decomposed.
4. Separator, to segregate condensed materials (powder) from gaseous phase. There are two technological streams after separator: powdery uranium oxide and gaseous phase carrying nitrogen oxides, water vapor, and oxygen.
5. Condenser-absorber, where the forced condensation of water, partial sorption of nitrogen oxides and nitric acid recombination takes place in the absorber. The resulted by-products are: distilled nitric acid solution, nitrogen oxides, nitrogen, and oxygen. To decontaminate the off-gas from nitrogen oxides to a required level, the extra sorption column may be installed.
6. Chemical composition of the powdery UO_x , the degree of HNO_3 - regeneration, and other parameters are defined primarily by the current plasma regime and by the method used for phase separation.

Fig.2 depicts schematically the physical and chemical transformation of the feed solution drops inside the chamber. At the first stage the drops are heated up to the boiling point and partially dried; the second stage is the complete water evaporation; and finally - overheating and decomposition of the salt residual.

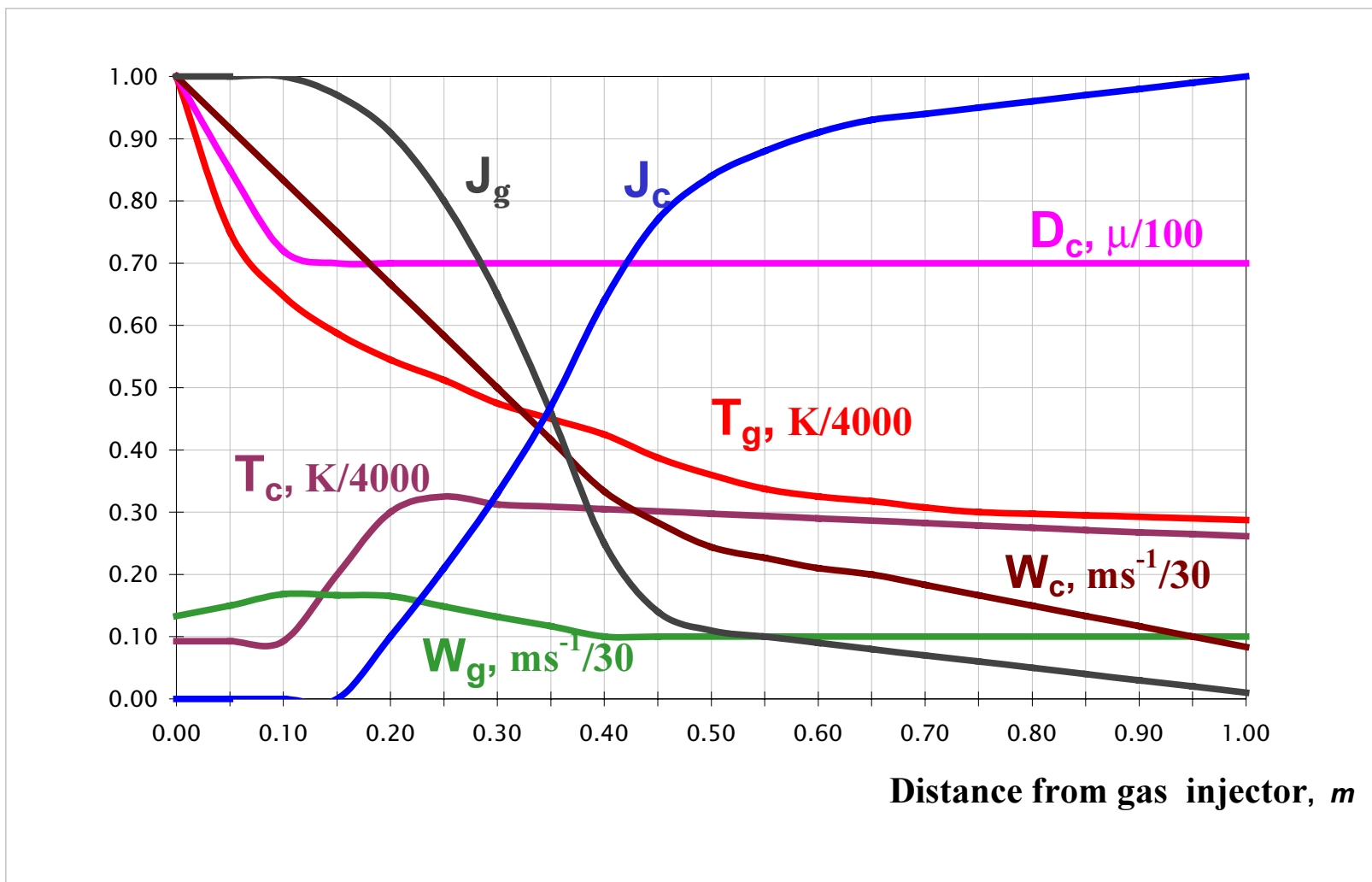


Figure 2. Change of process parameters at the decomposition of uranium nitrate solution in air plasma heat carrier.

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Development of the most expedient regime for plasma reprocessing is based upon the modeling of plasma reactor, also as on calculation and designing of its geometry - primarily the ratio of its length, L, and cross diameter, D, - to achieve the required way and decomposition rate of the source solution. Other principal requirements, as usually, are: low energy consumption and high coefficient of efficiency.

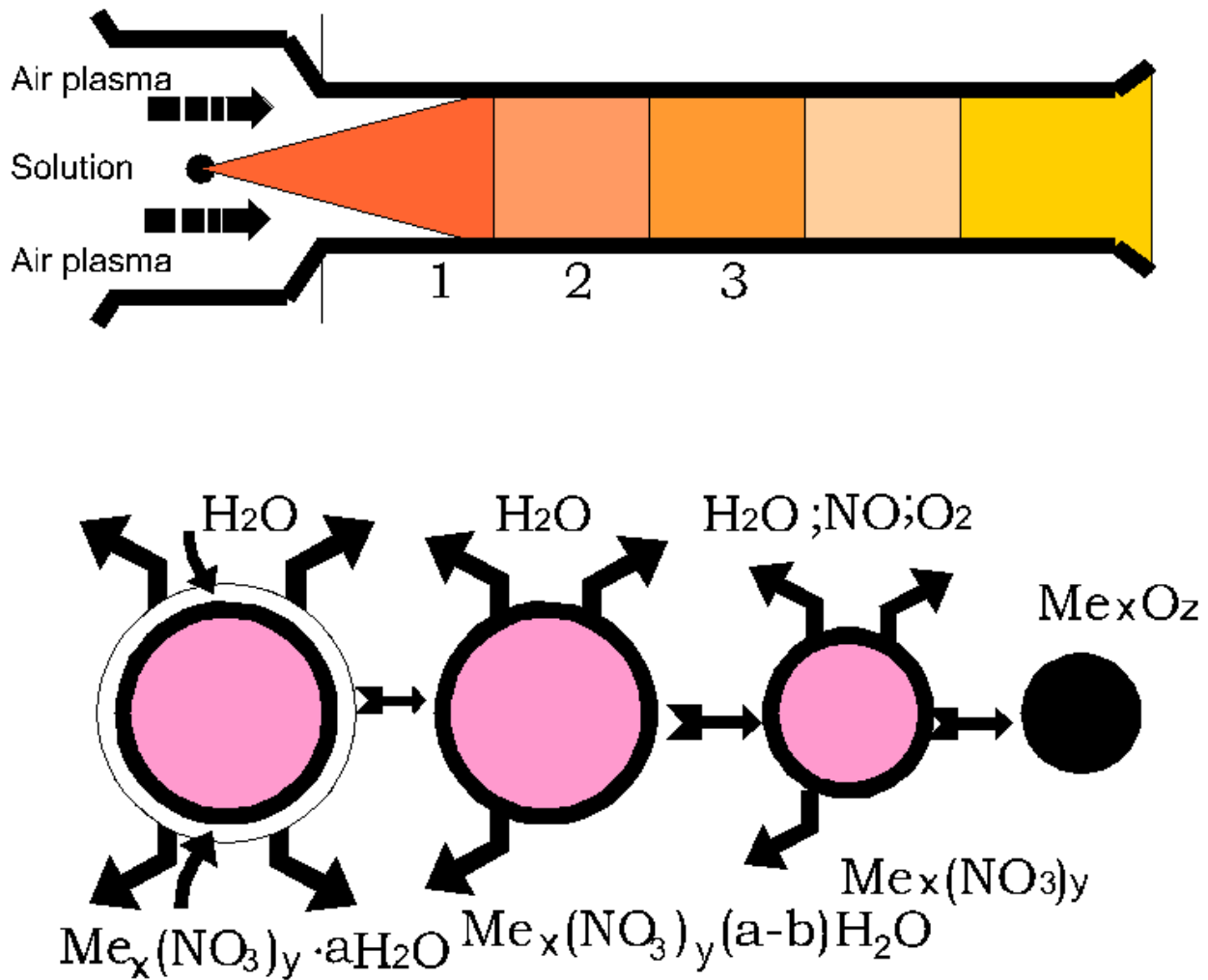
RESULTS AND DISCUSSION

The following parameters were chosen to model the plasma converter:

- electrical power of plasma torch (PT), kW	100-4000;
- start PT temperature, K	4000-6000;
- start drop diameter(D_d), m	20-200;
- start speed of the drops coming to reactor chamber (W_k), m/s	30-300
- feed solution consumption, kg/s	0,015-0,23;
- uranium concentration in feed solution, g/l	50-500

The principal results of the modeling are shown in Fig.3. The Figure shows the changing parameters of the plasma heat-carrier and of the dispersed powder in the two-phase stream along the reactor, for uniform distribution of the feed solution in the air/plasma heat-carrier. These dependencies allow to define the length of the reactor providing the desirable chemical composition, final temperature of heat-carrier, speed of gaseous and condensed stream, a diameter of final particles - supposing that secondary and consequent subdivision does not happen. Overall time of complete conversion may be estimated too.

Figure 3



1. - Heating of the drops up to \hat{O}_k .

2. - Solvent evaporation to the nuclei
 $Me_x(NO_3)_y \cdot (a-b)H_2O$ formation.

3. - Thermodecomposition of the nucleus- Me_xO_z .

The zone of complete decomposition of uranyl nitrate - up to 99% - has a length of 0.95 m. A temperature of the heat-carrier inside the plasma torch dramatically reduces with water evaporation, and increases a little with the torch diameter. The calculation has shown, that the length of evaporation zone rises with growth of the initial velocity of the drops, W_d , and their size, D_d .

We used the results of the simulated modeling (based on the above-stated relations) to design the plasma reactor for production of powdery oxide materials. An adequacy of the determined model was checked up experimentally. The test was carried out using the integrated technical parameters of the reactor and plasma process, indicated in Table 1.

Table 1.

Comparison of model calculations with experimental results for decomposition of uranyl nitrate solution

Experimental conditions

Electric power, kW/h	300;
Heat-carrier consumption, kg/s	0,016;
Heat-carrier temperature of, K	4000;
Feed solution consumption of, kg/s	0.02;
Specific energy consumption, kW*h per 1 kg of feed sol.	2.2;
Uranium concentration in feed solution, g/l	270;
Initial temperature of feed solution, K	293;
Initial velocity of drops, m/s	30;
Reactor diameter, m	0.3;
Average median diameter of drops, μ	150-200.

II. Results of comparison

Analyzed parameters	Results	
	model	experimental
Initial velocity of drops, m/s	150 - 200	150 - 200
Reactor length, m	1.76 - 2.0	1.8 - 2.5
Extent of conversion (to the aim products)	0.998 - 0.998	0,996 - 0,996
Heat lost - through walls of reactor, %	21.8 - 30.7	21,0 - 28.5
Gas-off temperature	1620 - 1500	1500 - 1470

The data show that the error in determination of the integrated parameters of a plasma conversion process is less than 20%, approving the adequacy of the developed mathematical model. The experimentally produced batches of powdery uranium oxide have the following size distribution (see Table 2).

Table 2.

Distribution of UO_x particles in size

Particle size, μ	Fraction, %
< 0,5	21
0,5-1,0	26
1,0-2,0	31
2,0-4,0	19
> 4,0	3
Specific surface of the powder, m^2/g	5,5
Bulky density, g/cm^3 (no shaking down)	0,69
(shaking down)	1,46

Then the powder was chemically reduced, sintered, and used for pellets fabrication.

The plasma denitration technique also was used for manufacturing of lengthy High Temperature Super Conductors (HTSC). The bench-scale process was demonstrated in two bench-scale plasma sets of power 100 and 300 kW; the appropriate input solution productivity was 25 and 50 l of an input solution per hour.

While the demonstration, a technological regime was worked-out to reconcile cationic compositions of the source solution and the final HTSC powder. Due to high temperature, the specific productivity is higher than the specific productivity of competitive methods, reaching 30-60 g/kW*h. HTSC ceramics of different type were produced:

$YBa_2Cu_3O_x$, $YBa_2Cu_4O_x$, and $Sr_2Ca_2Cu_3O_x$.

The Y-Ba-Cu ceramics have the following parameters:

bulky density, g/cm^3	0,5-0,7
«median» particle size d 50%, m	1-3
specific density, m^2/g	1-5
residual H_2O content, mass %	0,5-0,8
carbon concentration, mass %	0,1-0,2

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For the Bi-ceramics, the bulk density and the «median» particle size were: 0,7-1,0 «median» particle size, and $d_{50\%} = 3-6 \mu\text{m}$, appropriately.

The plasmachemical powders have high chemical activity: on annealing the Y-powders of «1-2-3» type, a content of $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase in 5 minutes exceeds 70 mass. % of the required value, while the process temperature is 50-100°C lower than for alternate techniques. Concentration of the «1-2-3» phase achieves 97% in 3 hours, while a carbon content is below 0.01%.

Determination of electrical and physical properties of the annealed powders has revealed a superconducting transition for Y-based composition, at $T = 90-95^\circ\text{C}$ ($\Delta T < 3^\circ\text{C}$), and for Bi-based mixture, $T = 108-109^\circ\text{C}$ ($\Delta T < 6^\circ\text{C}$). The polycrystal HTSC samples have a critical current, J_c , in a zero field near 300 A/cm² (Y-Ba-Cu), and 300-450 A/cm² (Bi-Sr-Cu).

Efficient plasmachemical technique for the production of special grade magnesia (MgO) was developed and successfully demonstrated in a pilot scale. The produced magnesia is applicable for protective coating of steel bars in electrical transformers.

Nowadays such magnesia is not produced in Russia. Main consumers of this oxide are: Verkh-Isetsky Metallurgical Plant (VIMP) in Ekaterinburg and Novo-Lipetsky Metallurgical Combine (NLMC) in Lipetsk. The magnesia of special grade is imported to Russia mainly from Japan ("Tateho Chemical") and Germany ("Lehmann")

The principal essence of the developed technique is plasmachemical decomposition of the source magnesium nitrate resulted by high-quality MgO and HNO₃- solution. Nitric acid is recycled back to the dissolution of the raw material - caustic magnesite.

Physical and Chemical Properties of Magnesia

Parameter	«Tateho Chemical» (Japan)	«Lehmann» (Germany)	«Plastech» (Russia)
Content, % mass.:			
· MgO	99,0-99,5	93,0-97,0	99,5
· C	-	0,7-1,0	-
· CaO	0,25	0,7-1,1	0,25
· Cl	0,02-0,04	0,02-0,03	-
· Fe ₂ O ₃	0,02-0,03	0,08	0,08
(insoluble in HCL)	0,01-0,02	0,04-0,05	0,01
Bulky Density, g/cm ³	0,24-0,25	0,12-0,15	0,15-0,30
Grain composition:			
· up to 3 m	80	40	95
· 3-5 m	20	60	5
«Lemon» number (CAA), c	60-80	25-35	60-120

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The proposed technique is ecologically clean and practically no-waste process.

Plasmachemical «denitration» method was also applied to produce another metal oxides (see below).

Zirconium, Aluminium, Chromium, and Zinc Oxides:

- chemical formula:	ZrO ₂ , Al ₂ O ₃ , Cr ₂ O ₃ , ZnO;
- average particle size, m	0,1-5,0;
- specific surface, m ² /g	3,0-40,0.

Chemical composition of oxide materials as well as their physical properties, regeneration rate for nitric acid and other parameters are determined by the process regime.

It is important to note:

- the developed plasmachemical approach provide a synthesis of different products of required parameters;
- the technique safely prevents any subsidiary harmful environmental effects.

CONCLUSIONS

1. On the basis of the developed mathematical model the laboratory plasma converter was tested and the complete thermal decomposition of a uranyl nitrate solution up to «yellow cake», U₃O₈ and nitric acid was demonstrated;
2. Comparison of the thermodynamic calculations with experimental results for uranyl nitrate decomposition has confirmed an adequacy with the determined mathematical model;
3. The plasma technique was successfully used to transform nitric acid salts of other metals - such as Mg, Y, Ca, Zn, Zr, Bi, Sr, Pb, Ba and their mixtures - to high-quality oxides.