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PLASMA-CHEMICAL PROCESSING OF MINERALS AND INDUSTRIAL WASTE

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ABSTRACT

Results are presented of the authors' investigations on plasma-chemical processing, under conditions of electric arc thermal plasma, of minerals (zircon, natural phosphates, bulgarite, serpentinite, pyrite), industrial concentrates (manganese oxide, molybdenum, cobalt cake) and industrial waste – solid (phosphogypsum, and refuse from Medet Company), liquid (waste of organics production) and gaseous (chimney gas from Thermo-Electric Power Stations, chemical and metallurgical enterprises, etc.). Processes of plasma-chemical production of nano-dispersed powders (NDP) are reviewed, namely plasma re-condensation (zircon, corundum), plasma destruction and/or reduction of zircon, manganese oxides, molybdenum compounds (molybdenum concentrate, molybdenum oxides), cobalt cake, iron-bearing compounds, etc. Design of electric-arc plasmotrons, plasma-chemical reactors and mixers, quenching devices and powder collectors is presented. A mechanism has been proposed for the plasma-chemical production of nano-dispersed powders (NDP) under conditions of high-enthalpy plasma jets. Production of NDP (metals – Mn, Mo, Co, Fe, oxides, nitrides, pigments, catalysts, etc.) is reviewed, which NDP are of practical interest (for example – in different contactors production, in powder metallurgy, chemical industry, machine-building, etc.).

INTRODUCTION

Plasma-chemical processing of different minerals, concentrates and industrial waste has been increased recently (Vissokov, 1984, 1987, 1998). The interest of investigators and users to this processing method is predetermined by the indisputable advantages of the plasma-chemical processes (PCP): 1. These processes proceed with high rate (contact time of $10^{-5} \div 10^{-3}$ s) at high specific enthalpies and high temperatures – all these factors lead to a miniaturization of plasma-technology equipment; 2. Most of the interesting from the practical point of view PCP are one-stage processes; PCP are practically insensitive to the admixtures in the raw materials; 4. PCP can be used to process difficult for processing but widely spread raw materials (air, ores, industrial waste, etc.); 5. PCP can be used to utilize valuable components from inorganic and organic chemistry production, from metallurgy at simultaneous waste destruction to non-harmful products that do not pollute the environment; 6. PCP can be easily modeled, optimized and controlled. Gas and electrodynamical controlling methods can be applied. This type of control leads to decreased thermal stability requirements for the plasma-chemical (PC) equipment; 7. All PCP can be organized in a similar technological scheme. The principal scheme of the PC equipment, independently on the PCP used, consists of low-temperature plasma (LTP) generator (plasmotron), mixer, plasma-chemical reactor (PCR), quenching device and a device for collection and separation of final products. 8. The plasma-chemical treatment does nor require big capital investment; 9. Uniform treatment can be achieved.

Goals of the present work were:

1. To summarize our investigations on plasma-chemical processing, under conditions of electric arc thermal plasma, of minerals, industrial concentrates and industrial waste – solid, liquid and gaseous.

2. To summarize the results of studies on plasma-chemical synthesis of nano-dispersed powders (NDP) by plasma re-condensation and plasma destruction and/or reduction.

3. To review the equipment (our design and preparation) for different electric-arc plasmotrons, plasma-chemical reactors and mixers, quenching devices and powder collectors.

EXPERIMENTAL EQUIPMENT

The following equipment has been designed and constructed (Vissokov, 1984):

- Electric arc plasmotrons – with two and many sections, with the capacity from several to 15 kW;
- Plasma-chemical mixers – cylindrical, truncated cone, etc.;
- Plasma-chemical reactors (metal and ceramic) – with "cold walls" (CW) – temperature of the wall T_{cw} = 500 K and with "warm walls" (WW) – temperature of the wall T_{ww} = 1500 K;
- Powder collecting devices: cyclones, sleeve-filters, electrical filters, etc.

A principal scheme of a plasma installation used for processing of minerals and industrial waste is presented in Fig.

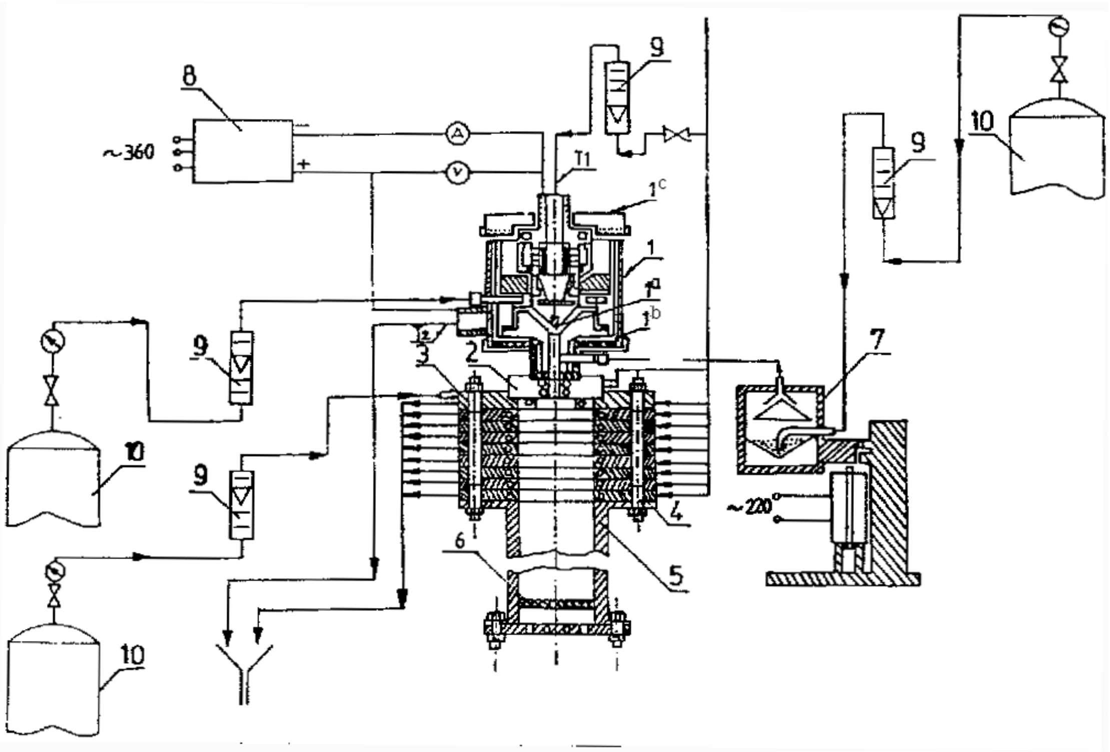

Figure 1. Schematic drawing of the plasma-chemical installation
1 - electric-arc D.C. plasmatron, 1^a – thoriated tungsten cathode, 1^b – copper water-cooled anode, 1^c – plastic adjusting ring, 2 – CW PCR, 3 – quenching device, 4 – copper water-cooled sections for the quenching device, 5 – powder-trapping chamber, 6 – filter, 7 – vibration powder-feeding device (if necessary, a piston type vibration powder-feeding device can also be used), 8 – current rectifier, 9 – flow-meters, 10 – bottles with plasma-forming, powder carrying and quenching gases, T_1 – temperature of inlet water, T_2 – temperature of outlet water.

RESULTS AND DISCUSSION

Model and thermodynamic calculations

Three-dimensional models of the motion, heating, melting, and evaporation (thermal destruction) of micron-size particles in an axial-symmetric PCR were developed. The models give the opportunity to determine the optimal parameters of the PCR: dimensions of the reactor, residence time of particles in the reactor, temperature in the PCR (CW) and PCR (WW), changes in particles size along the PCR, etc. The models allowed also obtaining the rate, density and temperature profiles of the plasma (gas) in the PCR, as well as parameters characterizing the motion, heating, melting and evaporation / thermal destruction of micron-sized particles in the PCR. Good correlation was found between model calculations and experimental results (Vissokov, 1998).

Thermodynamic equilibria calculations in multi-component systems are based on the fact that the Gibbs free energy reaches an extremum at the equilibrium. An isolated system (not exchanging mass and energy with the surroundings) was considered. Thermodynamic calculations were made at pressure of 0.1 MPa within the 1000÷3700 K interval (step of 300 K) at ratio solid phase / gaseous phase = 100 g/m^3. The following materials were considered as raw materials: natural phosphate, phosphogypsum, phosphite from Marocco, pyrite concentrate, refuse from Medet Company, bulgarite, serpentinite. Different mass ratios of ingredients were applied (Vissokov, 1984, 1998). The following components were considered in the solid phase (depending on the composition and ratio of ingredients): CaO, $CaSO_4$, Ca_2SiO_4, $Ca_2Al_2SiO_7$, CaF_2, $Ca_{10}F_2(PO_4)_6$, $Ca_2F_2O_5$, $Ca_3(PO_4)_2$, FeO, Al_2O_3, $CaMgSiO_4$, etc. The following components were considered in gaseous phase: S, SO, SO_2, SiO, Ca, CaO, CO, CO_2, PO, PO_2, F, MgF_2.

Experimental investigations on the plasma-chemical processing of minerals and industrial waste

Plasma destruction of minerals and concentrates

Thermal destruction of zircon was carried out (Vissokov, 1998) using the installation shown in Fig. 1. The crystal lattice of zircon was destroyed at temperature higher than 2050 K and a mixture of oxides was obtained:

$$ZrSiO_4 \Leftrightarrow ZrO_2 + SiO_2 \qquad (1).$$

The mixture was treated with 50 % solution of NaOH at temperature of 530 K. As a result, the amorphous SiO_2 was transformed into soluble salt:

$$SiO_2 + 2NaOH \Leftrightarrow Na_2SiO_3 + H_2O \qquad (2),$$

and ZrO_2 (grade of 95-96 %) was left in the precipitate. Even without SiO_2 leaching, the mixture of ZrO_2 and SiO_2 can be used for coloring the thermally resistant ceramics, as refractory and/or abrasive material, for chemicals production, etc. Materials made of ZrO_2 are heat-resistant up to 3000 K and those made of ZrO_2 produced by destruction – up to 2000 K.

Plasma destruction of Mn and Fe minerals (wustite, magnetite, hematite, and manganese oxide concentrate) turned to be an effective method for their transformation to inferior compounds (oxides, for example). Destruction of the lowest-valence oxides (MnO, FeO) to the corresponding chemical element and oxygen represents the limiting stage of the thermal destruction of the minerals.

Plasma-chemical re-condensation of high-melting-point substances is a method for producing nano-dispersed powders (NDP) (Vissokov, 1998). Nano-dispersed Al_2O_3 with specific surface of 30 ÷ 50 m^2/g (depending on the plasma-process conditions) was obtained by re-condensation of corundum (α-Al_2O_3) with particles size less than 50 μm.

Plasma-chemical reduction of ores and concentrates

The plasma-chemical reduction of metal oxide and metal sulfide concentrates (cakes) represents a new direction in the technology for processing metal-bearing raw materials and residues. Nano-dispersed metal powders (Mn, Mo, Co) have been obtained for the first time worldwide by reduction of corresponding concentrates (manganese oxide, molybdenum, cobalt cake) (Vissokov, 1998) under conditions of electric arc LTP at laboratory and/or pilot scale with use of gaseous reductants (H_2, C_4H_{10}, NH_3). Nano-dispersed Fe (with specific surface up to 160 m^2/g) was obtained by reduction of Fe_2O_3 with H_2, and the ratio α-Fe/γ-Fe can be controlled by changing the quenching rate.

Investigations on reduction of Co cake are presented here as an example. The Co cake is residue by-product of the Zn production by means of electrolysis of lead-zinc concentrates. The cake usually contains the following metals (in mass %): Co 2÷6, Zn 9÷11.5, Ni 0.0007÷0.0009, Cu 0.1÷1.0, and Cd 0.16÷0.5. Cake with the following composition was considered in our investigations aimed at increasing the Co amount in the cake (in mass %): Co 4.02, Zn 11.2, Ni 0.0007, Cu 0.72, Cd 0.16, and S 25.5. The cake enrichment with Co by means of plasma chemical reduction is based on the reaction:

$$CoS + H_2 \Leftrightarrow Co + H_2S \qquad (3).$$

Thermodynamic calculations for the reaction were made. Standard enthalpies of the substances participating in the reaction were used. Their aggregate state at corresponding temperatures was used in calculations. Results are presented in Table 1.

Based on the results shown in Table 1, it can be stated that from the thermodynamics point of view, the reduction of CoS with H_2 under the conditions of LTP has to be carried out in the temperature range of 1500 ÷ 2500 K.

Table 1. Temperature dependencies of the Gibbs free energy and equilibrium constant for the reaction (3)

T, K	1000	1500	2000	2500	2000	3500	4000
$\Delta G_T.10^3$, J/mol	7.53	-64.4	-33.8	-3.17	4.25	16.8	29.4
lgK_p	-1.64	9.39	3.69	0.277	-0.309	-1.05	-1.61
K_p	$2.3.10^{-2}$	$2.55.10^{9}$	$4.9.10^{3}$	1.9	0.49	$8.9.10^{-2}$	$4.05.10^{-2}$

Similar calculations were made for other components of the cake, which components can be reduced more easily. By drying at 500 K the cake was transformed into black powder with the following composition (in mass %): Co 6.08, Zn 16.9, Ni 0.0011, Cu 1.08, Cd 0.24, and S 19.9. The powder was plasma-chemically treated in the installation shown in Fig. 1. Results from chemical analysis (Co content, degree of reduction) and specific surface determination are presented in Figs. 2 ÷4.

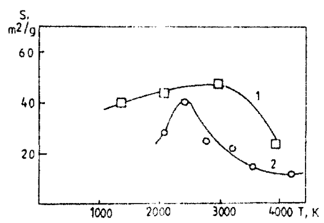

Figure 2. Specific surface (dispersity) as function of the average mass temperature of the plasma: 1 – at H_2 flow of 1540 L/h, 2 – at H_2 flow of 770 L/h.

The maximum in Figs. 2 ÷ 4 could be explained with the influence of opposite processes. The maximum observed in Fig. 2 could be assigned to the action of the following factors: a) as the share of the process taking place in gaseous phase

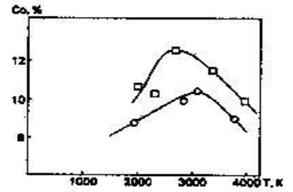

Figure 3. Co content in the product obtained as function of the average mass temperature of the plasma: 1 – at H_2 flow of 1540 L/h, 2 – at H_2 flow of 770 L/h.

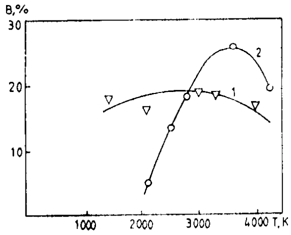

Figure 4. Reduction degree as function of the average mass temperature of the plasma: 1 – at H_2 flow of 1540 L/h, 2 – at H_2 flow of 770 L/h.

increases with the temperature increase, the specific surface of the product obtained also increases, and b) as the temperature increases, the process of NDP sintering in the dust-collecting chamber is enhanced and that leads to a decrease in the specific surface. The maximum observed increases with the temperature increase, the specific surface of the product obtained also increases, and b) as the temperature increases, the process of NDP sintering in the dust-collecting chamber is enhanced and that leads to a decrease in the specific surface. The maximum observed for the dependence “Co content / average mass temperature in the reactor” is moved to higher temperature at increasing the reductant flow (Fig. 3), because the reductant is used as powder-carrying gas and its movement decreases the average mass temperature in the PCR. The maximum observed for the dependence “degree of reduction of Co cake/ average mass temperature” depends also on the reductant flow (Fig. 4). At higher flow, the temperature in the reaction zone of the PCR decreases and as a result the equilibrium is moved to the left (towards sulfide). A mechanism with the following stages can be proposed to describe the process of Co cake reduction in H_2 medium: 1) heating the cake particles (predominately sulfides of Co, Zn, Cu, Cd and Ni) up to the melting point – heterogeneous reduction of sulfides takes place at that stage; 2) spheroidization of nearly-melted particles; 3) particles melting and formation of spherical drops; the drops are formed at constant temperature (melting temperature) and their size is gradually decreasing due to the evaporation; 4) entire evaporation of particles and substance transition to gaseous phase (under the form of atoms and radicals) – at temperature of 4000 K; processes of homogeneous reduction take place; 5) particles condensation in different phases during the quenching. Intensive reduction takes place during the first four stages (up to 4000 K). Conditions for the reverse reaction, described by equation (3) are created in the fifth stage, depending on the quenching effectiveness.

X-ray analysis of the products obtained showed that the Co is under the form of elemental Co, CoO and CoS. This finding shows the high chemical activity of Co powder obtained by means of reduction under the conditions of LTP – the air oxygen easily oxidizes the metal.

Experiments have been carried out to reduce the Co cake with Ar-H_2 plasma using Ar as powder-carrier. Results are presented in Table 2.

Table 2. Technological parameters for the plasma-chemical reduction of Co cake

I A	U V	W kW	Ar_{pl} L/h	$H2_{pl}$ L/h	Ar_{pc} L/h	Co %	S m^2/g	$S_{residual}$ %	B %
200	54	10.8	2550	390	340	11	36	18.26	8
300	55	16.5	2550	390	340	10.2	28	14.49	27.1

As it can be seen in the Table 2, compared to Figs. 2 ÷ 4, results for Co cake reduction by means of H_2 and Ar – H_2 plasma do not differ considerably. It has to be pointed out that Co powder concentrate containing about 20 mass % of Co and practically non-bearing S was obtained in pilot-plant installation using Ar – H_2 mixture and plasma-forming gas (Vissokov, 1998). This concentrate can be used to produce pure Co or Co compounds.

The main properties (such as specific surface, dispersity, degree of reduction, pyrophority, etc.) of the NDP, obtained by reduction, can be explained with the influence of the plasma-chemical process parameters and structural and chemical changes in the treated raw materials. Nano-dispersed metal powders (NDMP) obtained by plasma reduction of metal oxide and/or metal sulfide concentrates are characterized with their high specific surface (from several to several tens m^2/g), respectively - size of their predominately spherical particles – from several to 100 nm. The high dispersity of NDMP depends mainly on two factors: degree of raw material evaporation in the PCR and quenching effectiveness. The degree of raw material reduction depends on: material composition, temperature, kinetics of the corresponding reduction reaction (residence time in the PCR), quenching rate, effectiveness of the inhibition of the high chemical activity of the plasma-chemically synthesized NDMP. Physicochemical parameters of these powders can be controlled in a wide range by varying the parameters of the PCP.

The plasma-chemical production of NDMP (Mn, Mo, Co, Fe) can be of significant practical interest (for powder metallurgy, production of different Mo contactors, etc.), if raw materials with suitable composition are used and effective measures for NDMP passivation are taken. Suitable passivators were found (Vissokov, 1998) for decreasing the high chemical activity (pyrophority) of NDMP: N_2 – for Mn powder, CO – for Mo powder, and N_2 + 0.5% O_2 – for Fe powder.

Plasma-chemical oxidation of chemical compounds, ores and concentrates

High-energy parameters of the electric arc LTP represent an effective factor for obtaining NDP of different materials, such as: SiO_2 (by hydrolysis and oxidation of $SiCl_4$ or by oxidation and destructive evaporation of quartz sand), Al_2O_3 (by oxidation of elemental Al with O_2), Fe oxide pigments (by oxidation of coarse Fe and pyrite dross), metal oxides (by oxidation of corresponding metal concentrates, such as manganese oxide concentrate, etc.). To find the suitable temperature range of investigations, values of reaction enthalpy and equilibrium constant were preliminarily calculated.

Optimal conditions (temperature range, consumed power, flow, ratio of amounts of reagents used, place of reagents introduction into the reactor, shape of the reactor, type of the reactor – CW or WW etc.) of the PCP were determined in each case in order to ensure production of NDP and oxides with pre-determined characteristics.

Physicochemical properties (bulk mass, specific surface, chemical and phase composition, particles shape and size, purity, availability of admixtures, etc.) of the plasma-chemically-obtained NDP of SiO_2, Al_2O_3 and iron oxides have been studied. It has been found that a) the particles specific surface can be controlled in a wide range – from several to several hundreds m^2/g – depending on the PCP parameters; b) ND particles are with spherical or nearly spherical shape, their size is between 5 and 100 nm, the degree of monodispersity depends on the PCP parameters; c) the bulk mass, that depends on the dispersity of ND oxides, is in the range from several to several hundreds kg/m^3; d) admixtures in the ND oxide powders are due to admixtures in raw materials or (in some cases) to the erosion of electrodes or of PCR lining.

The phase analysis showed predominately availability of high-temperature thermodynamically unstable modifications of the corresponding oxides, except of the SiO_2 that was obtained as amorphous phase. The chemical composition of the nano-dispersed oxide powders (in the case when more than one oxide was obtained, iron oxides – as an example) is a function of the average mass temperature in the PCR (temperature profile of the reactor), over-stoichiometric amount of oxidizer and the reaction duration. The degree of raw material oxidation is determined by the thermodynamic and kinetic parameters of the corresponding process and by the process parameters, such as temperature, oxidizer concentration, time of the contact between the raw material and the oxidizer.

A mechanism has been proposed to explain the availability of high temperature thermodynamically unstable modifications of oxides that form NDP depending on the plasma process parameters and quenching effectiveness (Vissokov, 1998).

A technology has been developed for plasma-chemical synthesis of ND SiO_2 by reduction-oxidation process of quartz sand evaporation. A pilot plant (with capacity of 5 t/annum) was built on the territory of Himko-Vratza (Vissokov, 1998).

The plasma-chemically-synthesized ND oxide powders can be applied widely, as it follows: ND SiO_2 – as filler in pharmaceutical, cosmetical, food, and rubber industry, etc.; ND Al_2O_3 – as inert filler, adsorbent, heat- and corrosion-resistant material, in powder metallurgy, etc.; ND iron oxide pigments – for mineral pigments production (black, dark brown, brown, yellow, violet); and ND metal oxide concentrates – for producing the corresponding metals (Co, Zn, Mn) and their oxides and other compounds.

Plasma-chemical deactivation and utilization of solid, liquid and gaseous waste

Literature survey and experimental studies have been carried out on the plasma-chemical destruction (deactivation) of solid (expired pesticides), liquid organic (petroleum residues, pitch organic residues) and gaseous (CO_2, NO_x, SO_2, H_2S, industrial smoke, etc.) waste (Vissokov, 1984, 1987).

Solid and liquid organic waste is destroyed mainly under conditions of electric arc LTP. High-calorific combustible gases are obtained at that. Pesticides are rendered harmless under conditions of water electric arc LTP. Gaseous toxic oxides are plasma-chemically treated under conditions of corona discharge of different types of electrical filters. Nitrogen fertilizers are obtained as final product.

CONCLUSION

Summarizing the results of our investigations on the plasma-chemical processing of minerals and industrial waste, it could be pointed out that the plasma-chemical method proved to be effective in two main cases: a) when it is impossible products with specific characteristics (ND powders and/or oxides with high purity) to be obtained by conventional methods, and b) highly toxic solid, liquid and gaseous waste is to be deactivated and/or destroyed in a safe way.

REFERENCES

Vissokov, G., 1984. *Applied plasma chemistry, part 1, Application of low temperature plasma in inorganic chemical technology*, Sofia, *Tehnika*.

Vissokov, G., 1987. *Applied plasma chemistry, part 2, Application of low temperature plasma in organic chemical technology and metallurgy,* Sofia, *Tehnika*.

Vissokov, G., Pirgov, P., 1998. *Ultra-dispersed powders – plasma-chemical production and properties,* Sofia, *Poliprint*.

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