

Mechanism of the emergence and formation of powder particles during autoclave deposition of copper from sulphate solutions

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During the treatment of sulphate solutions containing 20-80g/l of copper with hydrogen at  $P_{H_2} = 20-30$  atm and 130-150°C the copper is deposited in the form of a powder at a rate of 0.5-0.3g/l. min.<sup>-1</sup>. The autoclave deposition of copper is characterised by the following features<sup>1, 2, 3, 4, 5</sup>:

a) In addition to the preferred formation of powdered copper in the volume of the pulp, part of it is deposited on the internal surface of the autoclave and on the moving parts of the mixing equipment, and this leads to blockage of the reaction volume, imbalance in the rotating components, and significantly complicates the long-term use of the equipment;

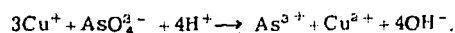
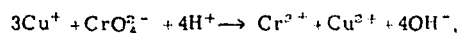
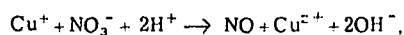
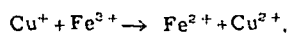
b) The degree of deposition of the powder increases with increase in the process rate (particularly at elevated temperatures) and decreases with the addition of surfactants of the polyacrylamide (PAA) type, i.e. the polymerisation products from acrylic acid;

c) The form and degree of dispersion of the particles depend on the temperature, the number of consolidation cycles, the salt composition of the solutions, and the type of surfactant;

d) The formation of monovalent copper ions in the intermediate stage.

Determination of the nature of the generation and formation of the particles of copper will make it possible not only to control the deposition of powder with specific characteristics but also to restrict the deposition of copper on the internal surfaces of the reactor. There are hardly any published data on these problems. In the present work, based on earlier<sup>2, 3</sup> and supplementary investigations, an attempt is made to fill this gap.

In view of the determining role of  $Cu^+$  ions the mechanism of the generation of the metallic phase<sup>1</sup>, it is right to suppose that copper powder should not form in the presence of additions which oxidise the copper ions or combine them into insoluble compounds (e.g. the chloride  $L_S = 1.02 \cdot 10^{-5}$ ). In experiments with oxidising agents containing ions having variable valence ( $Fe^{3+}$ ,  $NO_3^-$ ,  $CrO_4^{2-}$ ,  $AsO_4^{3-}$ ) there was an induction period, during which the content of copper in the solution hardly decreased at all. This was due to the following processes:

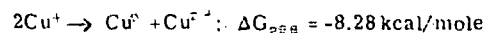


In the absence of copper, with other conditions equal, the composition of the solutions did not change during the treatment of solutions of ammonium ferrisulphate, nitrate, chromate and others.

With an increasing addition of chlorides ( $NH_4Cl$ ,  $NaCl$ ,  $KCl$ ) to the initial solution the deposition of copper on the reactor walls was reduced, while the chlorine content of the powder increased; with an equimolar (to the copper) and higher consumption of chloride ions, copper was not detected either on the reactor walls or in the metallic copper deposit. By X-ray diffraction it was established that the precipitate represented the compound  $CuCl$ . The addition of chloride ions did not affect the rate of decoppering of the solution.

Thus, experiments with oxidising agents and chloride ions confirmed convincingly that the generation of the metallic phase takes place through a stage involving the formation of cuprous ions. The subsequent discharge of the cuprous ions is more probable from energy stand-

points on account of the spontaneous development of the disproportionation process.



The equilibrium concentration of monovalent copper under the conditions of the investigated process is given by the equation<sup>3</sup>:

$$[Cu^+] = \left[ \frac{[Cu^{2+}]}{4.575 \exp \left( \frac{4650}{T} - 9.14 \right)} \right]^{0.5}$$

and does not depend on the concentration of hydrogen ions. Its value is small and when  $C_{Cu^{2+}}^0 = 0.5$ g-ion/l at 140°C, for example, amounts to only 0.06g-ion/l. To judge from the variation in the concentration of chloride ions combined with the  $Cu^+$  ions and also from published data<sup>2, 3, 6</sup>, the content of cuprous ions formed during the autoclave treatment of the solutions with hydrogen is considerably greater than the equilibrium content. Moreover, the properties of the powders (form, particle size, lattice constant) obtained by the autoclave deposition of copper ( $\tau = 10$  min,  $P_{H_2} = 38$  atm, 140°C) and on account of disproportionation in the  $Cu-Cu^{2+}$  system ( $\tau = 60$  min, 140°C) are quite comparable.

Thus, during the autoclave deposition of copper the metallic phase is formed as a result of disproportionation of the excess (above the equilibrium content) monovalent copper.

The unstable structure of the copper particles at the moment of generation during disproportionation, due to their excess surface energy, leads to approach of the particles to the distance characteristic of the crystal lattice and to 'condensation' of the metallic atoms in a direction perpendicular to the surface of the solid phase. As a result of the physical and chemical inhomogeneity of the solid surface, conditions are created on it for the formation of polycrystalline deposits on account of adhesion, and this increases with increase in temperature. (The formation rate of the disperse particles of copper increases). The adhesion of the copper powder to the reactor walls and to the surface of the mixing equipment, in the operating zone of which the generation of the energetically unstable crystalline particles mainly occurs, can be fully explained from these standpoints.

Table 1: Data on the specific deposition of copper (g/cm<sup>2</sup>) on certain solid materials with (I) and without (II) additions of PAA.  $C_{Cu}^0 = 68$ g/l,  $t = 140^\circ C$ ,  $C_{(NH_4)_2SO_4} = 100$ g/l,  $P_{H_2} = 28$  atm,  $C_{PAA} = 0.4$ g/l.

Name of material	I	II
Titanium (VT1-0)	0.021 (0.027)	0.059 (0.073)
Steel (EI-943)	0.014 (0.019)	0.046 (0.057)
Fluoroplastic (4M)	0.022	0.023
Graphite	0.074 (0.092)	0.056 (0.129)
Copper (M00)	0.046	0.064
Molybdenum	(0.064)	(0.122)
Tungsten	0.041 (0.078)	0.058 (0.109)
Corundum	0.064 (0.068)	0.045 (0.103)
Lead	0.042 (0.053)	0.048 (0.053)
Tantalum	0.043	0.059 (0.053)

Note: The data from experiments without the addition of ammonium sulphate are given in brackets.

27 To determine the effect of the nature of the solid surface on the process we determined the amount of copper deposited on plates ( $S_p = 12\text{cm}^2$ ) of various materials (table 1). Increased deposits of copper are brought about by contact release (Mo, W) and physical (graphite, corundum) or chemical (Ti, Pb, Ta) inhomogeneity. The copper deposits are appreciably reduced in the presence of ammonium sulphate and particularly with the addition of polyacrylamide. Without the anticoinciding additions powder deposits were observed even in the first 5-10 min after the beginning of the experiment.

In aqueous solutions titanium is normally coated with a film of hydrated dioxide, which has a well-developed specific surface and adsorption characteristics. The probability of solid-phase interaction in the  $\text{Cu-TiO}_2 \cdot n\text{H}_2\text{O}$  system is insignificant, since the structure and lattice constants of copper (cubic,  $a = 3.615\text{\AA}$ ) and titanium (tetragonal,  $a = 4.501\text{\AA}$ ,  $c = 2.9\text{\AA}$ ) are different. A chemisorption mechanism of adsorption of copper ions by hydrated titanium dioxide from the neutral solutions is more likely<sup>(14)</sup>. Thus, with the addition of  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$  to the initial solution at rates of 5-50g/l the amount of copper deposited on the reactor walls was reduced in proportion to the consumption of the additive. Thus, the deposition of copper on the reactor walls was due to the physicochemical inhomogeneity of the solid surface, which increases even more in the presence of surfactant films (in the case of hydrated titanium dioxide).

To reduce the powder deposits it was necessary to inhibit the internal surface of the reactor and to create conditions for the generation of particles of copper in the volume of the solution. The addition of organic substances was most favourable for this purpose. By the use of more than 50 types of ionic and non-ionic additives it was established that soluble poly-electrolytes (polymers based on acrylic acid and its derivatives) have the greatest anticoinciding effect. The carboxyl groups of these substances form hydrogen bonds with the hydroxyl groups of the hydrated titanium oxide film as a result of its hydrophilicity and of the preferred adsorption of high molecular compounds<sup>(11-13)</sup>. In our opinion inhibition of the reactor walls with the addition of surfactants is possible on account of saturation of the electronic vacancies and neutralisation of the surface charge. In addition, the carboxyl groups, which possess ion-exchange characteristics, form stable associations with the cuprous ions. On account of the micellar nature of solutions of poly-electrolytes, centres with an increased concentration of copper ions, in which reduction to cuprous ions takes place under the influence of hydrogen, are generated in the volume of the solutions<sup>(15)</sup>. On the attainment of a limiting concentration the cuprous ions disproportionate to form metallic copper. The rate of the above-mentioned processes increases with increase in the  $\text{Cu}^{2+}$  concentration and temperature, and this leads to an increased yield of the fine particles of powder. The further development of the process obeys the laws of sorption kinetics and depends on the characteristics of the active groups on the additives employed.

When the solution contains cations possessing increased sorption capacity, i.e. a greater charge, a smaller ionic radius as, for example, in  $\text{Fe}^{3+}$  and  $\text{H}^+$ , the conditions for preferred sorption of  $\text{Cu}^{2+}$  ions are impaired, and this leads to an increase in the amount of deposited copper on the internal surface of the reactor. The decrease in the deposition rate of copper when the solution contains oxidising agents is due to a decrease in the concentration of cuprous ions subject to disproportionation. The accumulation of acid in the solution, particularly at temperatures above  $150^\circ\text{C}$ , leads to disruption in the action of the organic additive. This is why the deposition of copper becomes more appreciable towards the end of the operation. The 'sorption' mechanism for the reduction of cuprous ions is also valid for inorganic sorbents. On account of their lower capacity, however, their role is of secondary significance and only shows up when the organic functional groups are

destroyed.

With an identical concentration of cuprous ions in the volume of the solution the conditions for their delivery to the various sections of the surface of the growing metallic copper, formed during disproportionation, should be identical, and this should predetermine the formation of equiaxial particles. However, the degree of dispersion and the shape of the particles of the obtained powders depend significantly on the nature of the surfactant<sup>(6)</sup> and the salt background of the solution<sup>(5)</sup>.

By being adsorbed on the surface of the growing copper, additions of surfactants reduce the surface tension, and this according to Wulff's law alters the growth rate of the faces in proportion to their surface tension. The subsequent growth of the particles depends on the strength and uniformity of the adsorbed layer of surfactant, and this is determined by the chain length and the nature and orientation of the radical in the surfactant. Adsorption of uniform character assists the formation of particles with rounded form; with selective adsorption on individual faces of the growing crystal stronger development is observed in the free (unblocked by surfactant) faces, and this leads to a change in the shape of the powder particles. Fig. 1 shows the effect of certain surfactants on the shape of the powder particles. In addition, the adsorption of the surfactant leads to neutralisation of the surface energy of the particles (their screening and limitation in the number of contacts between them). The development of these processes, determined by the nature of the surfactant and the medium, limits the probability of adhesion of the particles to the solid surface, and this increases the degree of dispersion of the powder and further reduces the probability of its deposition on the reactor walls. When additives with clearly defined blocking characteristics are employed, aggregation of the individual particles of powder is possible as a result of the formation of polymeric bridges of adsorbed surfactant molecules. A similar effect is observed (fig. 2) in experiments with polyacrylamide and 'Magniflok 140'. This effect becomes stronger as the copper is deposited (table 2) particularly in many-cycle experiments<sup>(16)</sup>, and this leads to an increase in the yield of the coarse fractions of powder.

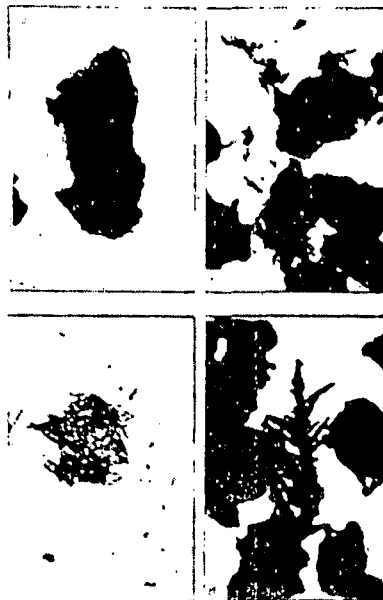


Fig. 1 The large-size fractions of the powders ( $+100\ \mu$ ) obtained from solutions containing, g/l: a) 5.0 polyacrylamide; b) and c) 0.4 granular, suspension polyacrylamide.

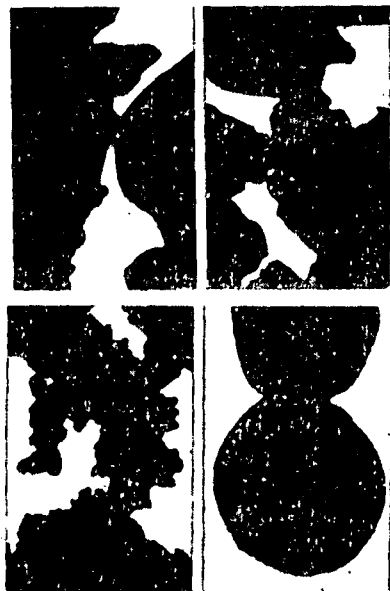


Fig. 2 Electron photomicrographs of the powders obtained with polyacrylamide (0.4 g/l).

Table 2: The properties of the powder as a function of the length of deposition.  $t = 150^\circ\text{C}$ ,  $P_{\text{H}_2} = 28 \text{ atm}$ ,  $C_{\text{Cu}}^0 = 60 \text{ g/l}$ ,  $C_{\text{PAA}} = 0.6 \text{ g/l}$ ,  $C_{(\text{NH}_4)_2\text{SO}_4} = 150 \text{ g/l}$

Deposition time min	Content (%) of fraction $\mu$				Specific surface area $\text{m}^2/\text{g}$
	+100	-100--74	-74--44	-44	
10	3.4	5.8	26.6	64.2	0.072
20	10.1	11.0	29.6	49.3	0.084
30	24.3	21.7	25.0	30.0	0.099

The character of the adsorption of the surfactant depends on the salt concentration of the solution. The cations of inert salts having a charge opposite to the charge of the functional group of the surfactant suppresses the dissociation of the surfactant and leads to closer packing in the adsorption layer. While also possessing increased hydration, the cations give rise to partial dehydration of the surfactant. As a result the ions of the surfactant become more hydrophobic and are adsorbed on the particles of the powder. This effect becomes stronger with increase in the polarisability and with decrease in the hydration of the cations.

According to these characteristics the monovalent cations can be arranged in the order Na, K,  $\text{NH}_4$  and divalent cations in the order Ni, Zn,  $\text{Fe}^{2+}$ . In these series a decrease in the degree of dispersion of the powder<sup>5)</sup> for a surfactant concentration of 0.4g/l was observed.

The orientation of the nuclei changes and their aggregation decreases under the influence of the electrostatic field of the cations<sup>1,6)</sup>. Here, the higher the strength of the field, the more likely the formation of dispersed particles. Thus, added inert metal sulphates affect the shape and degree of dispersion of the particles of powder both directly and on account of change in the adsorption of the surfactant.

The investigations demonstrate the considerable effect of organic additives on the mechanism of the deposition of powder on the walls of the reactor and also on the formation and growth of the particles of copper.

#### References

- 1) D I Evans: Advance extractive in hydrometallurgy: London 1967, p. 831.
- 2) S S Naboichenko: Tsvetnye Metally 1971, (1), 26.
- 3) S S Naboichenko: TsIN Tsvetnaya Metallurgiya 1971, (13), 27.
- 4) S S Naboichenko: Poroshkovaya Metallurgiya 1972, (4), 1.
- 5) S E Klyain et alia: Poroshkovaya Metallurgiya 1973, (7), 27.
- 6) S S Naboichenko et alia: Poroshkovaya Metallurgiya 1975, (10), 8.
- 7) E A von Hahn and E Peters: J. Phys. Chem. 1965, 69, (2), 547.
- 8) S E Klyain et alia: Izv VUZ Tsvetnaya Metallurgiya 1974, (4), 27.
- 9) G M Zhabrova and Yu V Egorov: Uspekhi Khimii 1961, 30, (6), 764.
- 10) I Riskin and T Velikostavinskaya: Zh. Prikl. Khim. 1969, 42, (6), 1400.
- 11) I D Kulikova et alia: in Macromolecules at the phase boundary: (editor Yu S Lipatov), Naukova Dumka, Kiev 1971, p. 86.
- 12) I Callum and C T Rankin: J. Polymer. Sci. 1971, 9, (10), 751.
- 13) A A Berlin and V E Basin: Principles of the adhesion of polymers: Khimiya, Moscow 1974.
- 14) V P Vasil'ev et alia: Zh. Fiz. Khim. 1960, 34, 1763.
- 15) Yu A Til'mans: Crystallisation of salts from aqueous solutions in the presence of various ions as impurities: Frunze, Akad. Nauk KirgSSR 1957.

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#### Electron ion exchange properties of mixed nickel and thallium ferrocyanide

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The separation of thallium from solutions with complex compositions in the form of mixed ferrocyanides of thallium and transition metals is characterised by its high selectivity<sup>1)</sup>. However, there is significant disadvantage in this process: the ferrocyanide only serves for one cycle and is thermally destroyed after saturation with thallium (the thallium is leached from the cake with water). The aim of the present work was to investigate the possibility of the desorption of thallium from the ferrocyanide without decomposition and to outline ways of regenerating the ferrocyanide sorbent. The search was based on the oxidation-reduction reactions involving ferrocyanides, which have already made it possible to obtain favourable results in the desorption of rubidium from analogous sorbents<sup>2)</sup>.

The investigation was carried out with samples of ferro-

cyanides having the following compositions:  $\text{Tl}_{1.10}\text{Ni}_{1.45}\text{Fe}(\text{CN})_6$  (sample A);  $\text{Tl}_{1.10}\text{Ni}_{1.45}\text{Fe}(\text{CN})_6 \cdot 0.25\text{Tl}_2\text{SO}_4$  (sample B). The first of them was obtained by ion-exchange saturation of the ferrocyanide  $\text{K}_{1.00}\text{Ni}_{1.50}\text{Fe}(\text{CN})_6$  with thallium from a 0.02N solution of  $\text{TlNO}_3$ . To prepare the second sample the same ferrocyanide was used as the starting material, but it was saturated with thallium from a 0.02N solution of  $\text{Tl}_2\text{SO}_4$ ; this led not only to ion exchange but also to molecular sorption of thallium sulphate. Solutions with the following compositions were used as oxidising agents: 0.1N  $\text{Ce}(\text{SO}_4)_2 + 1\text{N H}_2\text{SO}_4$ ; 0.1N  $\text{KMnO}_4 + 1\text{N H}_2\text{SO}_4$  (in individual experiments  $\text{H}_2\text{SO}_4$  was replaced by HCl); 0.1M  $\text{NaClO} + \text{CH}_3\text{COOH}$  (pH = 4). The oxidation was performed in airtight vessels.

The results showed that a considerable part of the thallium ions and a small amount of nickel ions pass from the