

REACTIONAL ELECTROLYSIS – EFFECTIVE METHOD FOR PURIFICATION OF METALS

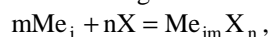
L.F. Kozin, F.D. Manilevich

*Institute of General and Inorganic Chemistry,
Ukrainian National Academy of Sciences,
32–34 prospekt Palladina, 03680 Kiev-142, Ukraine.
E-mail: fedor@ionc.kar.net*

The ability of generally used electrochemical refining as a method for purification of metals is limited. The total content of impurities in refined metal usually is not less than $1 \cdot 10^3$ %. For increasing the purity of metals obtained by electrochemical refining we proposed a new method which was named "reactional electrolysis". This method is based on using crude metals containing certain additives, as a rule, nonmetals. The introduction of such additives in crude metal is performed during melting anodes and leads to forming strong compounds of additives preferably with impurities. The formed compound must be insoluble or not readily soluble in water.

The thermodynamic analysis is used to choose such additives. The free energy of formation of additive compounds with impurities and with basic metal is evaluated. The more negative free energy values of the formed compounds with impurities than with basic metal give evidence of preferable formation of impurity compounds. The binding of impurities into strong compounds leads to decrease of thermodynamic and hence electrochemical activity of the impurities. Therefore selected additives are considered as depressants of impurities. The electrode potentials of impurity compounds are significantly more positive, than potentials of the impurities, and bound impurities don't participate in anodic dissolution of crude metal, but form anode slime. As a result, impurities don't pass into electrolyte and don't participate in cathodic deposition of basic metal. The binding of basic metal with additives is negligible and, hence, its electrode potential remains practically unchanged.

The method of reactional electrolysis was applied to electrochemical refining of the following metals: lead, bismuth, cadmium, tin, indium, copper, iron, manganese, nickel. Sulfur, selenium, tellurium, silicon, boron, antimony were used as depressants. It should be noted that these depressants are effective in relation to metallic impurities because form strong compounds with them in accordance with the following reaction:



where Me_i = metal-impurity, X = element-depressant. In principle, metals also can be used as a depressant if they form not readily soluble intermetallic compounds with metallic impurities or strong covalent compounds with nonmetallic impurities.

As was shown, the compounds of additives with impurities often have a very low solubility in basic metal and therefore float to the surface of melted crude metal. This allows separating a part of impurities from basic metal before electrolysis.

Electrolyzers with filtering membranes were used for refining of mentioned metals by reactional electrolysis. The material of electrolyzers was acrylic resin.

Data about impurity contents in the some metals refined by reactional electrolysis is presented in the following tables. It is obvious, that reactional electrolysis

permits obtaining high purity metals, what cannot be made electrochemically without the above method.

Table 1. Impurity contents in refined cadmium

Impurity	Content (n·10 ⁸ %)	Impurity	Content (n·10 ⁸ %)
Au	0.3	Sn	200
Ag	5	Na	10
W	10	Cu	50
In	10	Cs	4
Ga	20	Pb	n.d.*
Co	5	Tl	n.d.*
As	5	Ni	<0.1
Se	2	Hg	n.d.*
Te	2	Al	n.d.*
Sr	2	Sb	<2
Zn	50	Bi	n.d.*
Fe	50	Mn	n.d.*
ΣMe_i 4.25·10 ⁻⁶ %			
Cd 99.999996 %			

*n.d. = not detected

Table 2. Impurity contents in crude and in refined tin and purification factors (α)

Impurity	Crude tin (n·10 ⁴ %)	Refined tin (n·10 ⁶ %)	α
Ag	8.5	6.4	133
Zn	1	<5	>20
Fe	38	<120	>32
Au	0.36	0.016	2250
As	12	<16	>75
Sb	19	<3	>633
Cd	–	<12	–
Sc	–	<0.01	–
Ga	0.2	<10	>2
Cu	9.1	<5	>182
ΣMe_i	88.16	6.416	1374
Sn 99.999994 %			

Table 3. Content of impurities in crude and in refined iron and purification factors

Impurity	Crude iron (n·10 ² %)	Refined iron (n·10 ⁵ %)	α
Mn	20	0.15	133333
Ni	4.4	1.4	3143
Cr	9	19	474
Co	1.5	2.4	625
Al	17	37	460
Mo	1.1	5.5	200
Cu	20	3.5	5714
Ti	0.5	4.6	109
ΣMe_i	73.5	73.55	999
Fe 99.9993 %			