

## **TECHNOLOGICAL ASPECTS REGARDING CHROMIUM VALORIFICATION FROM ELECTROPLATING SLUDGE FOR ENVIRONMENT DEPOLLUTION**

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**Abstract.** The paper presents some aspects regarding recovery and valorification of chromium from electroplating sludge. The electroplating sludge resulted from the neutralisation lines of washing waters and electroplating spent solutions from chromium electroplating lines of aeronautical industry. This sludge holds important amounts of chromium and another metals like sparingly soluble hydroxides, i. e. Cu, Ni, Zn, Cd, Fe, P, etc. It is stored on the plants and is regarded as an important source of environmental pollution. Therefore, the storage of this kind of sludge may contaminate the industrial platforms with toxic substances. The recovery of the chromium from this sludge is necessary firstly for elimination of environment pollution and then because of the necessity to bring back in economic circuit of chromium. Some electroplating sludge resulted from aeronautical platforms were characterised with respect to their chemical and mineralogical composition. The research which was carried out had as a goal the valorification of the chromium from this sludge like chromium pigments or chromium solutions for tanning. This paper presents average compositions of chromium sludge, the results obtained at the solubilisation phase of these sludge, the work conditions adopted for maximum efficiencies of solubilisation of chromium and some results obtained at the purification phase of the solution. A graphical representation was made in order to present the influence of some operation parameters on the solubilisation and purification efficiencies of chromium and others components of the sludge.

*Keywords:* electroplating sludge, chromium, recovery environmental depollution.

### **AIMS AND BACKGROUND**

The fast development and diversification of science and technique over the last twenty years, lead in the end to some undesired ecological and economical phenomena. The humanity was standing in a difficult situation: limited available reserves of raw materials, and exploitation by known and conventional technologies. One way to overcome this crisis could be reintroduction of reutilisable materials in economic circuit.

The appearance in Romania of the new environmental law (512/22, Oct. 1999), which is very restrictive regarding storage of the wastes containing heavy

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metals, leads to the accumulation of large quantities of toxic sludge on industrial platforms, creating many problems for environment.

One of these wastes is the sludge resulted from neutralisation stations of washing waters and spent solutions from electroplating lines. Their content in utile materials often exceeds the content of poor ores or complex composition, electroplating sludge being in the same time concentrated sources of raw materials and potential polluting factor of the environment.

From all electroplating tips used on various industrial platforms, the literature indicates chromium hardening like as the most spread.

The large utilisation of chromium is due to the properties of electrolitique chromium: chemical stabilisation, abrasion resistance and the double possibilities of electrodeposition on ferrous and nonferrous metals.

The chromium depositions have the following characteristics: heat proof, corrosion resistance due to formation of a protective film ( $\text{Cr}_2\text{O}_3$  inactive) and the hardness is much better than hard steel.

The valorification of chromium from electroplating sludge shows in this context a different interest.

Reduction of expenses necessary for accessible storage and prevention of environment pollution next to the recirculation in economic circuit of chromium from these sludge are good arguments to approach this subject in the context of development of recirculation wastes like a solution in the fight against environmental pollution.

The literature presents various procedures to recover chromium from industrial wastes<sup>1-4</sup>. The recuperation process of metals from this sludge has two processing phases:

- solubilisation of the metals which may be acid, alkaline or smelting with various salts;

- recovery (as a matter of fact ) of these metals in an economic re-use form.

Depending on the nature of the utilised reagent for the solubilisation of the metal, it will be in the solution in sulphate, nitrate, chloride, chromate or another form.

Because the acid solubilisation is more widely applied from the point of view of recovered metals and concerning recovery ways from solutions, this method was imposed much more in researcher view.

The separation of the metals from solubilisation can be done by applying various procedures presented in the literature like: chemical and electrochemical methods, precipitation (pp.), cementation, crystallisation, ion exchange, solvent extraction, etc.

Table 1 shows the pH range in which various metals from solutions precipitate.

**Table 1.** pH range in which metals from solution precipitate

Metallic ions	pH values			Substances for precipitation	Value established for complete pp. (mg/l)
	the beginning of the pp.	complete precipitation	dissolution of the pp.		
Fe <sup>3+</sup>	2.8	3.5	-	Ca(OH) <sub>2</sub> , NaOH, Na <sub>2</sub> CO <sub>3</sub>	2
Sn <sup>2+</sup>	3.9	colloidal	10.6	NaOH	-
Al <sup>3+</sup>	4.3	4.8	8.5	Ca(OH) <sub>2</sub> , NaOH	2
Cr <sup>3+</sup>	5.5	6.3-6.5	9.2	Ca(OH) <sub>2</sub> , NaOH, Na <sub>2</sub> CO <sub>3</sub>	2
Be <sup>2+</sup>	5.8	non determined	-	NaOH, Na <sub>2</sub> CO <sub>3</sub>	-
Cu <sup>2+</sup>	5.8	7.5	-	Ca(OH) <sub>2</sub> , NaOH	1
	5.8	8.5	-	Na <sub>2</sub> CO <sub>3</sub>	
Zn <sup>2+</sup>	7.6	8.3	>11	Ca(OH) <sub>2</sub> , NaOH	3
	7.6	8.3	-	Na <sub>2</sub> CO <sub>3</sub>	
	7.4	7.9	>11		
Fe <sup>2+</sup>	cca.9	cca.9	-	NaOH	-
Ni <sup>2+</sup>	7.8	9.3	-	Ca(OH) <sub>2</sub> , NaOH, Na <sub>2</sub> CO <sub>3</sub>	3
Pb <sup>2+</sup>	7.0	9.5		Ca(OH) <sub>2</sub> , NaOH	1
	5.5	6.5	9.1 colloidal	Na <sub>2</sub> CO <sub>3</sub>	
Cd <sup>2+</sup>	9.1	9.5...9.8	-	Ca(OH) <sub>2</sub> , NaOH	3
	7.0	7.2	-	Na <sub>2</sub> CO <sub>3</sub>	
Ag <sup>+</sup>	9.5	colloidal	-	NaOH, Na <sub>2</sub> CO <sub>3</sub>	-
	9.25	non determined			

## EXPERIMENTAL

The quantitative study of chromium valorification from sludge with this metal content was carried out starting from electroplating sludge resulted from the neutralisation station of Romania industrial aeronautical platform. Table 2 shows the chemical composition of the sludge for 5 samples taken over at various periods of times. The results of the analyses show that the sludge used for the experiments is a wet material with a high content of chromium between 4.5-5 % in wet sludge and 13-27 % in dry sludge with variable wet, with Cd, Fe, Al, Cu, Ni, Zn impurities.

X-ray diffraction analysis of the raw sludge reveals the presence of amorphous material such as hydrated oxides and heavy metals hydroxides.

Our studies were focused at studying: the acid solubilisation in order to bring metals from sludge in solution; the selective precipitation of the metals in the various pH range; the comparison of the results with literature indications.

**Table 2.** Spectral and chemical analyses of a sludge

Element	Spectral analysis	Chemical analysis				
		sample 1 (%) (wet material)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)
Cr	Z.P	4.29	14.72	16.04	18.27	20.68
Fe	0.5 – 1.0	0.24	3.92	0.96	0.89	0.32
Cd	0.5 – 1.0	0.035	<0.005	0.072	0.09	0.03
Pb	< 0.1	<0.005	<0.005	-	0.001	<0.005
Ca	0.5 – 1.0				0.75	
Si	10 <sup>-1</sup> – 5.10 <sup>-1</sup>	<0.002	<0.01	0.1	0.086	0.016
Na	5×10 <sup>-2</sup>				5.7	
Al	p	0.03	0.31	1.52	0.8	0.10
Cu	0.5 – 1	0.22	0.24	0.26	0.38	0.12
Zn	0.5 – 1	0.042	0.064	0.11	0.16	0.068
Ni	5×10 <sup>-1</sup>	0.043	0.30	0.12	0.072	0.018
Mg	5×10 <sup>-1</sup>	0.009	0.05	0.21	0.12	0.11
Ti	5×10 <sup>-2</sup>	0.009	0.026	0.028	0.024	<0.005
P	10 <sup>-3</sup>	0.6	13.20	14.29	1.45	0.47
Sn	10 <sup>-2</sup> – 5.10 <sup>-2</sup>	0.026	<0.005	0.096	0.15	0.026
Sb	5×10 <sup>-2</sup>	0.006	0.071	0.05	0.07	0.094
Anion:						
NH <sub>4</sub> <sup>+</sup>		0.10	0.12	-	0.21	0.18
Cl		<0.01	0.21		0.064	0.092
NO <sub>3</sub>		0.59	1.1	0.91	2.46	0.24
SO <sub>4</sub>		1.42	5.26	11.91	16.11	25.94
CO <sub>3</sub>		0.29	6.23	9.25	1.12	4.32
H <sub>2</sub> O		84.53	8.57	24.07	21.09	9.4
P.C. 800°C				39.39		
P.C.1000°C				1.35		

*Solubilisation of the sludge in acid medium, in an open system.* The experiments were carried out in a laboratory installation under the following conditions: continue stirring of the suspension; temperature between 20-80°C; normal pressure; acid concentration – 20 %; time for adding H<sub>2</sub>SO<sub>4</sub> – 45 min; 10-20% excess of H<sub>2</sub>SO<sub>4</sub> over stoichiometric quantity; S:L ratio 1:5-1:10; total time of reaction 2/4 h at the experimental temperature; final pH of 0.5-3.5.

The solubilisation efficiency of chromium and other metals and the compositions of the solutions were determined. Table 3 shows the results obtained in the experiments.

Table 3. Results obtained at the solubilisation of the sludge in an open system

No	Sludge Vol. intro-duced (g)	pH final	Time (h)	Temp. (°C)	Final volume (ml)	Composition of the solutions resulted at the solubilisation (g/l)							Solubilisation efficiencies (%)									
						Cr	Fe	Cd	Cu	Ni	Zn	Al	Si	Cr	Fe	Cd	Cu	Ni	Zn	Al	Si	
1	100	20	1.52	2	25	1033	12.6	0.13	0.03	0.13	0.05	0.07	1.33	0.08	81.5	14.1	47.5	51.6	41.3	63.8	90.5	87.8
2	100	20	2.87	2	40	1041	11.8	0.28	0.04	0.15	0.05	0.07	1.27	0.08	76.7	30.6	54.9	60.0	45.9	71.9	86.9	83.2
3	100	20	3.05	2	60	1038	10.9	0.24	0.03	0.13	0.05	0.07	1.12	0.08	70.3	25.9	47.6	51.9	40.6	79.9	76.5	79.9
4	100	30	1.62	2	25	1055	12.6	0.35	0.04	0.16	0.05	0.07	1.29	0.09	78.3	36.3	49.8	60.8	44.8	63.3	85.4	89.7
5	100	30	1.42	2	40	1052	14.1	0.41	0.04	0.15	0.05	0.08	1.33	0.09	93.1	44.5	41.6	60.7	45.5	73.6	92.1	87.3
6	100	40	0.86	2	25	1040	10.9	0.31	0.03	0.11	0.04	0.07	1.08	0.07	70.6	33.6	41.8	44.1	36.4	62.4	73.9	73.8
7	100	60	0.40	2	25	1060	12.3	0.38	0.02	0.09	0.04	0.05	1.28	0.06	81.5	41.9	35.3	39.1	33.6	47.2	89.3	61.5
8	100	60	1.58	2	40	990	14.1	0.41	0.03	0.10	0.04	0.05	1.24	0.06	87.1	42.3	48.4	37.3	32.2	45.9	80.7	57.4
9	100	60	0.1	4	70	980	13.5	0.43	0.04	0.15	0.05	0.07	1.26	0.08	81.3	43.9	49.0	56.5	43.9	66.8	79.9	80.0
10	100	60	0.1	2	80	970	12.9	0.42	0.04	0.15	0.05	0.08	1.23	0.08	70.2	39.4	44.5	52.2	38.8	63.5	70.8	55.3
11	100	30	2.3	2	40	1072	12.4	0.36	0.03	0.15	0.05	0.06	1.19	0.08	82.8	40.0	50.5	61.7	43.7	62.3	83.8	72.8
12	100	30	1.0	2	40	627	22.4	0.66	0.06	0.26	0.09	0.11	2.26	0.14	87.5	43.1	52.2	62.7	43.3	62.7	93.2	87.8

Observation: experiment 11 was realised in sulphato-ammonium medium and experiment 12 at S : L ratio = 1 : 5.

The influence of some reaction factors on the metals solubilisation efficiencies were also evaluated.

*Influence of temperature.* The experiments were carried out under the following conditions: temperature between 20-80°C; normal pressure; S:L ratio = 1:10; acid : sludge ratio = 1.66 – 5 (ml:g). Table 4 shows the results obtained as a function of the amount of sulphuric acid used.

**Table 4.** Influence of temperature on metals solubilisation efficiencies as a function of acid:sludge ratio

Work conditions	Solubilisation efficiency (%)							
	Cr	Fe	Cd	Cu	Ni	Zn	Al	Si
Temperature 25°C, sulphuric acid : sludge ratio = 1:5 ( ml : g)	81.5	14.1	47.5	51.6	41.3	63.8	90.5	87.8
Temperature 40°C, sulphuric acid : sludge ratio = 1:5 ( ml : g)	76.7	30.6	54.9	60.0	45.9	71.9	86.9	83.2
Temperature 60°C, sulphuric acid : sludge ratio = 1:5 ( ml : g)	70.3	25.9	47.6	51.9	40.6	79.9	76.5	79.9
Temperature 25°C, sulphuric acid : sludge ratio = 1:3.3 ( ml : g)	78.3	36.3	49.8	60.8	44.8	63.3	85.4	89.7
Temperature 40°C, sulphuric acid : sludge ratio = 1: 3.3 (ml : g)	93.1	44.5	41.6	60.7	45.5	73.6	92.1	87.3
Temperature 25°C, sulphuric acid : sludge ratio = 1:1.66 (ml : g)	81.5	41.9	35.3	39.1	33.6	47.2	89.3	61.5
Temperature 40°C, sulphuric acid : sludge ratio = 1:1.66 (ml : g)	87.1	42.3	48.4	37.3	32.2	45.9	80.7	57.4
Temperature 70°C, sulphuric acid : sludge ratio = 1:1.66 (ml : g)	81.3	43.9	49.0	56.5	43.9	66.8	79.9	80.0
Temperature 80°C, sulphuric acid : sludge ratio = 1:1.66 ( ml : g)	70.2	39.4	44.5	52.2	38.8	63.5	70.8	55.3

It was observed that the solubilisation efficiency of the metals increases with temperature only if an excess of acid at the solubilisation is used.

At stoichiometric quantities of the acid, the solubilisation efficiency decreases with increase of the temperature. But in all cases the solubilisation efficiency of chromium was between 80-90 % and next to the chromium there are all other metals in solutions in various proportions.

*Influence of pH over solubilisation efficiency.* The experiments for sludge solubilisation were realised under the following terms: temperature 25°C; S:L ratio 1:10; time 2 h at work temperature; normal pressure (Table 5).

**Table 5.** Variation of metals solubilisation efficiency from the sludge as a function of sulphuric acid quantity at constant temperature

Work conditions	Solubilisation efficiency (%)							
	Cr	Fe	Cd	Cu	Ni	Zn	Al	Si
Temperature 25°C, acid : sludge ratio = 1 : 5	81.5	14.1	47.5	51.6	41.3	63.8	90.5	87.8
Temperature 25°C, acid : sludge ratio = 1 : 3.33	78.3	36.3	49.8	60.8	44.8	63.3	85.4	89.7
Temperature 25°C, acid : sludge ratio = 1 : 2.5	70.6	33.6	41.8	44.1	36.4	62.4	73.9	73.8
Temperature 25°C, acid : sludge ratio = 1 : 1.66	81.5	41.9	35.3	39.1	33.6	47.2	89.3	61.5
Temperature 40°C, acid : sludge ratio = 1 : 5	76.7	30.6	54.9	60.0	45.9	71.9	86.9	83.2
Temperature 40°C, acid : sludge ratio = 1 : 3.33	93.1	44.5	41.6	60.7	45.5	73.6	92.1	87.3
Temperature 40°C, acid : sludge ratio = 1 : 2.5	87.1	42.3	48.4	37.3	32.2	45.9	80.7	57.4

One can notice that a significant increase of sulphuric acid quantity at ambient temperature leads to an insignificant increase of solubilisation efficiency of chromium while the solubilisation efficiency of Fe increases very much and decreases for the other impurities.

The increase of the temperature up to 40°C has a positive influence on the solubilisation efficiency bringing it up to 93 %.

*Influence of reaction medium over solubilisation efficiency.* It is known that in ammonium-sulphate medium some metals form soluble complexes. Consequently, we tried to see how ammonium sulphate in acid reaction medium influences the solubilisation efficiency of metals. The work conditions and the operating procedure were the same as for the previous experiments (Table 6).

The analyses show that ammonium sulphate has a negative effect on the solubilisation efficiency, this medium favours the reprecipitation of chromium.

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In conclusion it is possible to affirm that when there is a lot of heavy metals in the solution together with chromium, the behaviour of these metals at precipitation is different from the situation when the metals are alone in solution.

## CONCLUSIONS

The research which was carried out had as a goal the maximum efficient solubilisation of chromium from electroplating sludge of aeronautical industry.

The physico-chemical and structural analyses of the raw sludge used for the experiments show a high content of chromium 13-27 % in dry sludge with Cd, Fe, Al, Cu, Ni, Zn impurities.

X-ray diffraction analysis reveals the presence of an amorphous material such as hydrated oxides and heavy metals hydroxides.

The experiments of solubilisation were realised for the beginning in an open system, in sulphuric acid or ammonium acid medium, in order to see the influence of some reaction factors on the metal's solubilisation efficiencies.

The solubilisation efficiency of chromium was between 80-93 % depending on the working conditions.

Together with chromium in the solution from solubilisation of the sludge there are some heavy metal impurities.

The solubilisation efficiency of sludge is optimum when the pH values are between 1.5-2.5. Within these pH values it is possible to obtain a high solubilisation efficiency for chromium and a first separation of Sn, Pb, P in residue.

The experiments carried out show that the chromium solubilisation in open system, with maximum efficiency, is possible under the following conditions:

- temperature 40 - 50°C;
- contact time 2 h;
- S:L ratio 1:5;
- final pH 2-2.5;
- acid medium;
- continue stirring.

In order to separate chromium from the solubilisation solution it was used alkaline precipitation with NaOH. In the first stage of precipitation in the interval of pH 3.3-3.5, chromium is separated instead of iron. During the precipitation, chromium involves other metal impurities. When there are other heavy metals in the solution next to chromium, the behaviour of these metals during precipitation is different from the situation when the metals are present alone in solution. Quantitative separation of chromium from solutions is possible under the following working conditions: temperature about 60°C; pH between 3.5-6.5.



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