Water Treatment and Detoxification of the By-products Resulted from Lubricating Phosphatation of Iron-Based Metal Parts

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The paper presents data from the application of a new waste water treatment and of detoxification of industrial by-products resulted from degreasing, pickling and phosphating processes of metal parts based on iron. As in the microcrystalline phosphating are involved a series of potentially high toxic substances and waste water have complex chemical and physical charge, for them and the resulting sludge was developed a procedure involving four competitive processes: classical coagulation, flocculation with a polyelectrolyte with high capacity of ion exchange (for anions and cations), adjustment of the optimal pH (8.5...9.5), and destabilization of the microcoloidal system by involving adsorbers type fly ashes. These processes are applied simultaneously in single step stations – only mechanically.

Keywords: waste waters treatment, detoxification, cristalline phosphating, slurries, coagulation systems, stereospecific flocculation

For detoxifying water and slurries containing heavy metal ions (Zn, Fe, Cu etc.), there are known a series of purification procedures by using loess or other adsorbers [1-3], involving precipitation, coagulation and flocculation processes [4-9] or by electrocoagulation processes [10, 11]. Also, there are known a number of water treatment procedures, containing orthophosphate anions, by precipitation with lime or calcium hydroxide [2, 3, 6]. They have the disadvantage of high costs due to the use of precipitation agents, such as orthophosphoric acid and its salts, which in turn introduces a new source of phosphate ion pollution.

There is known a denitrification and dephosphating procedure for waste water and depleted industrial by-products [3, 6, 8], by precipitating them with lime. This procedure has the disadvantage that the detoxification process is applied to diluted systems in nitrogen and phosphate ions, such as domestic waste waters. Moreover, for the purification of depleted industrial by-products it is applied a two-stage treatment procedure based on the resumption of precipitation and coagulation in an acid medium [2-9].

For purifying the industrial and domestic waste waters, with soluble chemical charge, inorganic (transition metal and ammonium cations, nitrate, nitrite, phosphate and sulfate anions) and organic (urea, phenol, detergents, dyes etc.), with insoluble or physical charge (mineral and organic suspensions) there are known several procedures in one single step [12-14], using various systems, alone or in conjunction, for example a classical coagulant based on Al(III) and/or Fe(III) [15], a flocculant polymer able of ion exchange, a pH regulator and a stereospecific destabilizator for the mycroheterogeneous systems.

These procedures have the disadvantage that they can not be used to separate detoxification of water resulting in precipitation and washing, and of slurries resulting from microcrystalline industrial phosphating processes of iron parts.

In this regard, the paper presents some experimental data on the degree of detoxification achieved after applying a new treating procedure for toxic components from industrial depleted by-products, which allows both wastewater treatment and detoxofication of slurries resulted in degreasing, pickling, microcrystalline lubricating phosphatation of metal parts based on iron.

Experimental part

Sources of pollution resulted in microcrystaline phosphating processes

In industrial practice there are used a series of microcrystalline phosphating procedures of iron-based metal parts by surface chemical passivation, in order to obtain on surfaces superficial thin colored layers, giving a certain aesthetic [16, 17] or those of high porosity capable of allowing insertion of lubricating solid structures, with multiple action to improve processing characteristics and implicit protection, with better adhesion to metal substrates based on iron [18-20].

In the first case of the phosphatation with purpose of obtaining polychrome and passivating surfaces, after degreasing and pickling, it is applied a two-step sequential chemical treatment [17]:

- first, it is deposited a thin porous layer of copper obtained by cementing or nickel by electrodeposition, as reactions:

$$\underline{Fe^0} + CuSO_4 \rightarrow \underline{Cu^0} + FeSO_4,$$
$$Ni^{2+} + 2e^- \text{ (cathodic deposition)} \rightarrow \underline{Ni^0}$$

- then follows the precipitation of copper orthophosphate or nickel respectively, by immersion in two acid aequous solutions, one with weak oxidizing character based on phosphate anion and Zn^{2+} cations, in the presence of permanganate anion as surface moderator and another based on orthophosphoric acid containing dispersed fine powder of metallic zinc applied different by immersion, at ambient temperature, on the cleaned surfaces, as reactions:

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$$\underline{15Cu^0}+6KMnO_4+16H_3PO_4 \rightarrow \underline{5Cu_3(PO_4)_2}+\underline{2Mn_3(PO_4)_2}+2K_3PO_4+24H_2O/$$
$$/3Zn^{2+} + 2K_3PO_4 \rightarrow \underline{Zn_3(PO_4)_2} + 6K^+$$
$$3x\underline{Cu^0} + 2(x+y)H_3PO_4 + 3y\underline{Zn^0} \rightarrow \underline{(Cu_x/Zn_y)_3\ (PO_4)_{2(x+y)}} + 3(x+y)H_2\uparrow.$$

The procedure is based on the phosphating process in acid medium throughout an *additive / substractive mechanism*, in which are implied metallic cations Cu, Zn, Ni and Mn, in various oxidation states, which become inert after precipitation according with Fe(0) in the substrate. These cations are both susceptible to acid-base and complexation processess, also redox, resulting thin porous films by coprecipitation as orthophosphates, even in the presence of oxidic or salt stains, poorly hydrated, based on Fe(II, III), which become soluble by mild oxidation in the presence of permanganate anion.

Both processes generate by-products (depleted solutions, washing waters and slurries) with toxic chemical charge due to the above transition metal cations, together with the iron cations, phosphate and sulphate anions.

When microcrystalline lubricating phosphatation takes place [18, 19], after degreasing and pickling, it is applied a sequential chemical treatment, in two stages too:

- first it is done the precipitation of iron orthophosphate in presence of nitrate ion and hydroxylamine sulphate (SHA) in acid medium, according to the reaction:

$$3\underline{Fe^0} + 2H_3PO_4 \xrightarrow{HNO_3/SHA} \underline{Fe_3(PO_4)_2} + 3H_2\uparrow,$$

- then, the interstition by coprecipitation of zinc orthophosphate is done, by immersion of the parts in orthophosphoric acid containing dispersed fine metallic zinc powder at 90°C, during 30 min, according to the reaction:

$$x\underline{Fe_3(PO_4)_2} + 3y\underline{Zn^0} + 2(x+y)H_3PO_4 \rightarrow (xFe/yZn)_3(PO_4)_{2(x+y)} + 3(x+y)H_2\uparrow.$$

In this case, the procedure is based on the process of phosphating in acid medium by a substractive/additive mechanism with insertion, in the presence of Zn^{2+} cations, following which, there is an uniform growing of crystals at a temperature of 90°C, forming dendritic patterns richly branched and veloured, with high retention of lubricating colloidal suspentions in aquous or organic systems. The resulting film is then coated in hydroalcoholic colloidal dispersion of graphite or molybdenum, steric and electrostatic stabilized in the presence of NH_4OH-NH_4Cl buffer system, which gives an optimal *p*H of 8.5...9.00.

In this case, both processes generate by-products with toxic chemical charge, yet containing only iron and zinc cations, traces of hydroxylamine, along with phosphate, sulfate and nitrate anions.

Wastewater treatment and detoxification of slurries

To detoxificate by-products resulted in processes described above, a new procedure of treatment was developed, in two sequences, the precipitation-washing of waters and slurries [21]. These by-products have a high chemical load both in anions (phosphate, sulfate, nitrate and chloride), as in cations too (zinc, iron, copper and manganese). In order to neutralize the heavy metals and the toxic anions, there are used a series of acid-base, redox processes, assisted by coprecipitation, consisting in two phases.

Treatment of wastewater resulted from washing and depleted solutions from phosphatation, by coprecipitation of transitional metals and of phosphate, sulfate and nitrate ions, using the microdisperse system of calcium hypochlorite 1...3% and 10% lime, at a ratio water/alkaline hypochlorite lime system varying between 100...500, depending on the chemical load, after which the treated solution is destabilized by adding mineral coagulant based on aluminium sulfate(III) – 4g/L and a polymeric flocculant based on cationic polyelectrolyte obtained by polycondensation of dimethilamine and triethiltetramine with epichlorhydrine with a concentration of 0.15...0.25%. To the microeterogen system is added fly ash (50g/L) with the purpose of agglomeration and to increase the sedimentation rate [3].

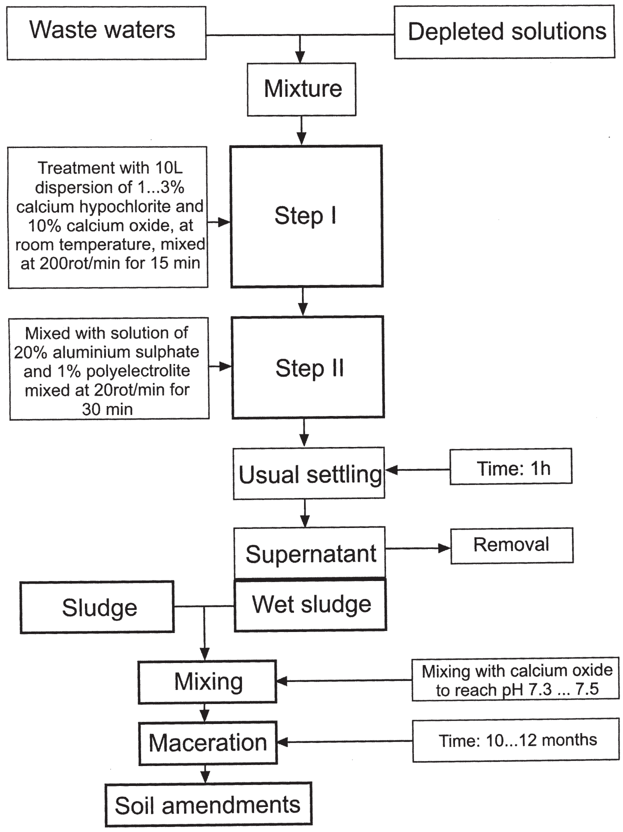

Fig. 1. Technological flow for wastewater treatment and detoxification of by-products resulted in crystalline phosphating of iron metal parts

From the treatment with calcium hydroxide and hypochlorite result mixed salts with cation in stable oxidation state, which are low soluble. Moreover, the floculant allows the precipitation of the soluble cations and anions [7].

After decanting, the precipitate is mixed with the slurry resulting from phosphatation and lime, in order to achieve a *p*H of 7.3...7.5. The mixture is kept to macerate on concrete platforms in the open air for 10...12 months, after which the solid product is used as soil amendments.

Thus, for 1m^3 wastewater mixture with depleted solutions, were used the following quantities of solutions and materials:

- 10 L dispersion containing 1...3% calcium hypochlorite and 10% calcium oxide (lime);
- 20 L solution of aluminium sulphate (III) 20%, containing 1% polyelectrolyte.

In the first stage, the mixture of waste waters and depleted solutions is treated with an oxidising alkaline solution at normal environment temperature, strong stirring (200 rpm) for 15 min then adding cuagulant and flocculant solution, gently shaking at a speed of 20 rpm for 30 min.

System is decanted for one hour, the clear solution is removed, then the wet slurry is mixed with the one resulted

Table 1

COMPOSITION OF THE DEGREASING SOLUTIONS

Chemical Components	Concentration, g/L	
	Initial Solution	After depletion
Sodium hydroxide, NaOH	40	8.5 (as HO^-)
Disodium carbonate, Na_2CO_3	30	15 (as CO_3^{2-})
Trisodium phosphate, $Na_3PO_4 \cdot 10H_2O$	30	18 (as PO_4^{3-})
Disodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$	5	2.5 (as SiO_3^{2-})
Detergent (surfactant)	3...10	2....5
Work parameters	**Value**	
Temperature, [°C]	80...90	15.....18
pH	11.0...12.0	9.0...9.5

Table 2

COMPOSITION OF THE PICKLING SOLUTIONS

Chemical Components	Concentration, g/L	
	Initial Solution	After depletion
Hydrochloric acid, HCl (ρ=1,19g/cm^3)	150.00	45.00
Hexametilentetramine, $C_6H_{12}N_4$	0,45	0.40
Disodium sulfate, decahydrat, $Na_2SO_4 \cdot 10H_2O$	0,15	0.50
Work parameters	**Value**	
Temperature, [°C]	20...25	18..20
pH	1...2	3.5

Table 3

COMPOSITION OF THE PHOSPHATATION SOLUTIONS IST

Chemical Components	Concentration, g/L	
	Initial Solution	After depletion
Copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$	125.00	15.50
Vegetal Tanning, (type Quebracho or Mimoză)	15.00	2.5
Sulfuric acid, H_2SO_4	few drops	-
Work parameters	**Value**	
Temperature, [°C]	50	18...20
pH	3,5...4	5.5...6.0

from phosphatation and also with lime, until the *p*H 7.3...7.5. The mixture is laid for maceration on concrete platforms in open air for 10...12 months, after which the solid product is used as soil amendment.

The technologic procedure for wastewater treatment and for the detoxification of the by-products resulted in the crystalline phosphating of iron metal parts involves attending several stages and phases, summarized in figure 1.

Techniques involved in determination of cations and anions

The chemical charge of wastewater and slurries resulted in the lubricating crystalline phosphating process and of slurries resulted after treating them for detoxification, consists in cations like: Na^+, K^+, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+}, anions: HO^-, Cl^-, CO_3^{2-}, PO_4^{3-}, SiO_3^{2-}, SO_4^{2-} and NO_3^- and a number of other chemical components: surfactant/ detergent, hexamethylenetetramine, tannine, poly-electrolite etc., in many varied concentrations. In the analysis of the two subsystems – solutions and slurries – were involved the following techniques, for solutions: digital pH-meter type PH 340i-SET, spectrophotometer type Colorimeter DR-850 and HACH DREL F800 as well as a Multiparameter HACH, while for slurries, after siccativating, drying and pelleting, they were analysed by SEM-EDX technique.

Results and discussions

From the technological processes of the two phosphatating procedures results four groups of wastewaters: from degreasing and pickling, and

Table 4

COMPOSITION OF THE PHOSPHATATION SOLUTIONS IIND

Chemical Components	Concentration, g/L	
	Initial Solution	After depletion
Orthophosphoric acid, H_3PO_4	135.00	26.50
Potassium permanganate, $KMnO_4$	16.00	6.0 (as Mn^{2+})
Zinc sulfate, $ZnSO_4$	162.00	8.20
Nitric acid, HNO3	4.0	0.05
Work parameters	**Value**	
Temperature, [°C]	20...25	18...20
pH	2.5...3.5	4.0...4.5

Table 5

CHEMICAL COMPOSITION OF WASTE WATER (MIXTURE SOLUTION)

Chemical Components	Concentration, g/L	
	Initial mixture solution	After treatment
Chlorure anion, Cl^-	12.20	0.25
Sulfate anion, SO_4^{2-}	31.20	0.18
Orthophosphoric anion, PO_4^{3-}	55.50	0.04
Metasilicate anion, SiO_3^{2-}	0.16	0.05
Carbonate anion, CO_3^{2-}		0.17
Nitrate anion, NO_3^-	0.021	0.002
Mn^{2+}	1.80	0.01
Zn^{2+}	27.10	0.005
Cu^{2+}	20.80	0.01
Fe^{2+}	33.50	0.05
Na^+	4,50	0.48
K^+	1.40	0.26
Work parameters	**Value**	
Temperature, [°C]	20...25	18...20
pH	2.5...3.5	6.5...8.0

Table 6

CHEMICAL COMPOSITION OF SLUDGE WASHING SOLUTION, BEFORE AND AFTER TREATMENT

Chemical Components	Concentration, g/L	
	Initial	After treatment
Cl^-	0.60	0.05
Mn^{2+}	0.18	0.01
Zn^{2+}	0.36	0.01
Cu^{2+}	0.12	0.02
Fe^{2+}	0.16	0.06
Na^+	0.35	0.11
K^+	0.20	0.06
Working parameters	**Value**	
Temperature, [°C]	20...25	18...20
pH	7.5...8.0	6.5...7.5

respectively from the two phosphatations (I and II). Based on material consumption established on laboratory facility with a 5 L capacity for the four groups of wastewaters, after 25 sets of 20 pieces (experimental samples) treated, the following volumes of solutions used resulted: 5 L wastewater solution after degreasing, 5 L waste water solution after pickling, 25 L wastewater solution after first phosphatation and 25 L wastewater solution after second phosphatation, altogether 60L of waste solution.

In tables 1, 2, 3 and 4 are presented the compositions of the four solutions, initially and after depletion.

Conclusions

In order to neutralize toxic ions, resulted from microcrystalline lubricant phosphating process, by the new procedure [21], are used acid-base processes, assisted by redox coprecipitation of transition metals cations and carbonate, sulfate, phosphate, silicate and nitrate anions.

The neutralization processes are done in two stages: first the treatment of waste waters resulted from washing and depleted solutions from phosphatation processes; the second is the treatment of the sludge resulted from the precipitation in the first treatment and from phosphatation.

The first treatment is done by coprecipitation of transitional metals cations and anions, using the microdispers system of calcium hypochlorite and lime, at a ratio waste water/alkaline system of 100...500. After that the treated solution is destabilised by adding mineral coagulant based on aluminum sulphate (III) and a flocculant polymer based on cationic polyelectrolyte (obtained by polycondensation of dimethylamine and trietiltetraminei with epichlorohydrin). After these processes the waste waters are decanted (usual settling) and the clear solution (supernatant) has a very low content in toxic ions.

In the second stage, to the mixt sludge lime is added, in order to achieve a *p*H of 7.3...7.5, followed by maceration for 10 ... 12 months on concrete platforms in the open air. After this, the resulted product is used as soil amendment.

From treated water and sludge analysis resulted that applying the present process provides a better treatment of waste water from the four stages of the process of phosphatation and a good detoxification of the sludge. The concentration of toxic transitional metals cations and anions is according to the 100 NTPA Standards, and can be spilled into the emissary.

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