Scientific Papers, UASVM Bucharest, Series A, Vol. LIII, 2010, ISSN 1222-5339

ECOLOGICAL CLOSURE OF THE SLIME DEPOSITION AT S.C. OȚEL INOX S.A. TÂRGOVIȘTE

NINETA RIZEA, R. LĂCĂTUŞU, LAZĂR RODICA

National Research and Development Institute for Soil Science, Agrochemistry and Environmental Protection of Bucharest

Keywords: *slime deposition, ecological closure*

Abstract

Slime deposition resulting from technological process of pickling steel bands is located in the unit S.C. OȚEL INOX S.A. Slime is a metal waste which cannot be recuperated and its storage in the deposition is final.

Because storage slime on deposition no. 3 approached to the final rate, the unit commanded a study necessary for the ecological closure of the slime deposition. By construction, slime is stored in a concrete pit which is a barrier for soluble salts and heavy metals to infiltration into the soil and underground water

To determine the chemical composition of slime deposition, there were collected several surface samples and a profile, uniformly distributed on the sides of deposition and on the ridge deposition.

From the surface, samples obtained an average sample used for the levigation test and the first eluate of the percolation test.

The analytical values determined for all the elements are within the range given by the Order 95/2005 and is not a danger of water pollution with chemical elements.

As a result, slime deposition no. 3 stored in the S.C. OȚEL INOX S.A. area containing pickling process slime can be subject to ecological closure, in accordance with the environmental legislation.

INTRODUCTION

The slime resulted of the technological process of pickling steel bands and all afferent operations that happen in S.C. OȚEL INOX S.A. Târgovişte (main activity - cold rolling) is stored in depositions located inside the company. The unit is located in an industrial area of the town Târgovişte, in the south-west of the town, besides the road no.16 to Găeşti.

The purpose of this study is the deposition no. 3 with a storage capacity by approximate 4750.2 m^3. Slime is a metal waste which can not be recuperated and its storage in the deposition is final. Slime deposition resulting from the technological process of pickling steel bands is located in the west of the unit S.C. OȚEL INOX S.A.

Slime deposition is protected by construction for the soil and subsoil pollution because it is stored in a concrete pit. Both floor and walls are constructed of reinforced concrete. The floor is provided with a grid to collect the liquid phase. Around the floor there is a sewer to collect rainwater and waters which derive from the slime.

Before storage, the slime on the pit a layer of lime was disposed in clods (with a thickness of about 20 cm) in order to produce a neutralization reaction with the stored slime.

Since storage slime on deposition no. 3 approached the final rate, unit S.C. OȚEL INOX S.A. Târgovişte commanded a study necessary for the ecological closure of the slime deposition, realized by I.C.P.A. Bucharest [1].

MATERIAL AND METHODS

To determine the chemical composition of the slime deposition no. 3, there were collected several samples of 7 points: 6 points (P1, P2, P3, P5, P6 and P7) were uniformly distributed on the sides of deposition and 1 point (point P4) was placed on the ridge deposition. Samples of the points P1, P2, P3, P4 and P7 were taken on 0-20 cm depth, the P6 point on 0-5 cm depth and a profile was made at the point P5 on 200 cm depth (4 samples).

From the surface, samples was obtained an average sample used for the levigation test L/S = 10 l/kg, and the first eluate of the percolation test C (0) L/S = 0.1 l/kg.

The analytical methods used for slime samples were: reaction, nitrates, total soluble salts content, soluble salts, heavy metals - total content and mobile forms, soluble and the total fluoride [3].

RESULTS AND DISCUSSION

The physical and chemical property of the slime

The freshly taken samples had gray to dark-gray colors. In the storage, slime is a semisolid material, predominantly yellow-rusty colors with black, rusty brown, reddish, orange, black to white spots or areas, due to the presence of the calcium hydroxide mixed with slime.

From the chemical point of view, slime is a mixture of oxides and hydroxides of heavy metals, emanated from chemical composition of metal bands. The chemical composition of slime include salts such as sulfates, chlorides, fluoride, resulted in the process of pickling neutralization technology.

The reaction of the slime samples was moderately alkaline in samples collected at the point P6 (pH = 8.90) and strongly alkaline in the point P1 (pH = 9.78). For the other slime samples reaction was extremely alkaline with values within pH range = 10.36-11.20 (Table 1).

Slime high alkalinity is due to the calcium hydroxide solution (10%) used in the precipitation processes of the heavy metals, and to a mixture of salts containing sodium hydroxide (62.2%) used in the thermochemical pickling process. The slime reaction over pH=10 indicates that in the neutralization process was used an excess of the hydroxide calcium.

The lower amount of moisture to the surface samples was 50% (P6, 0-5 cm) and the highest was 85% (P2, representing the newly deposited material) (Table 1). For profile samples (P5), slime humidity ranged between 74% and 79%.

The total content of the soluble salts have similar values in the surface horizons and the profile slime, being in the range 1301-2082 mg/100g (mean values = 1661 mg/100g) and corresponds to a strong salinization compared with the limits concerning the soils salinization degree.

The salinization was mainly sulphatic, and anionic and cationic composition of the soluble salts showed that the dominant salts are: calcium sulfate and calcium nitrate, then sodium nitrate and calcium chloride. Small quantities of calcium bicarbonate, magnesium nitrate and potassium nitrate occur.

The sulfates were formed in the pH correction process of the wastewater to a value of 2-2.5 pH units with sulfuric acid (neutralization station). Chlorides were formed along the entire process. Nitrates were resulted from chemical and electrochemical pickling with nitric acid.

The calcium and sodium salts were formed in the precipitation processes of heavy metals with calcium hydroxide solution (10%). In the thermochemical pickling process was used a salt mixture containing 62.2% sodium hydroxide, 25% sodium nitrate and 12.5% sodium chloride (neutralization station).

Soluble fluorine values were between 36 and 47 mg/kg with a mean of 42 mg/kg. The total fluorine content varied between 1.6% and 2.6%, with the mean of 2.1% (Table 1).

The total and mobile content of heavy metals presented approaching values in the surface horizons and the profile.

Because the chemical elements determined in slime samples had generally similar values in the, surface horizons and the profile, show that slime have a similar composition, even if the collection was made on the surface or in depth deposition.

The levigation test and first eluate of the percolation test

The concentrations of the chemical elements in P1 - the levigation test L/S = 10 l/kg and P2 - C (0) - first eluate of the percolation test L/S = 0.1 l/kg) were presented in Table 2.

The P1 reaction is moderately alkaline (pH = 9.03) and it is given by the presence of the sodium carbonate. The P2 reaction is slightly alkaline (pH = 8.22) and is due to the calcium bicarbonate.

Table 1

Chemical analysis of surface samples from slime deposition no.3

Indicator	Unit	Values					
		P1	P2	P3	P4	P6	P7
pH	pH units	9.78	10.85	10.77	11.20	8.90	10.36
Water extract, ratio 1:5							
HCO_3^-	mg/100g	35	44	49	43	32	44
Cl^-	mg/100g	75	41	24	53	60	76
SO_4^{2-}	mg/100g	499	356	24	309	24	380
NO_3^-	mg/100g	632	760	970	530	1462	1005
Ca^{2+}	mg/100g	415	322	243	269	457	434
Mg^{2+}	mg/100g	2.2	0.8	0.7	0.5	7	1.5
Na^+	mg/100g	61	115	48	93	38	102
K^+	mg/100g	4	4	3	4	3	4
Total soluble salt content	mg/100g	1723	1643	1362	1301	2082	2047
F, total	%	2.1	1.6	2.5	2.0	2.6	2.1
F, soluble	mg/kg s.u.	39	42	36	39	41	47
Heavy metals, total forms							
Zn	ppm	39.6	35.2	39.6	36.0	41.9	31.7
Cu	ppm	127	133	127	122	197	122
Fe	ppm	90041	108936	114493	108936	110418	97451
Mn	ppm	992	1258	1487	1293	1275	1134
Pb	ppm	34.9	42.1	56.7	34.9	42.1	71.2
Ni	ppm	7111	6595	8069	8290	9469	7995
Cr	ppm	13157	15493	35031	18891	16130	17617
Co	ppm	184	186	215	211	239	192
Cd	ppm	*	*	*	0.15	*	*
Heavy metals, mobile forms							
Zn	ppm	0.66	1.75	1.63	1.34	1.50	1.31
Cu	ppm	19.0	67.1	43.5	40.2	32.7	42.6
Fe	ppm	9.29	5.71	3.93	3.57	10.0	3.93
Mn	ppm	80.8	87.3	74.3	87.3	77.0	61.3
Pb	ppm	4.22	8.58	6.40	4.22	3.49	4.22
Ni	ppm	624	353	611	641	1054	731
Cr	ppm	349	327	667	520	789	496
Co	ppm	7	6	8	10	16	12
Cd	ppm	*	*	*	*	*	*

* values under detection limit

Calcium salts predominated, followed by sodium salts pursuant to the precipitation processes of heavy metals with calcium hydroxide 10% and the usage of a mixture of sodium salts in the thermochemical pickling process.

The content of heavy metals in the levigation sample P1 is low. The analytical values determined for all the elements are within the range given by the *Order 95/2005* [2] and there is no danger of water pollution with those chemical elements.

By construction, slime is stored in a concrete pit which is a barrier for soluble salts and heavy metals to infiltration into the soil and underground water. During storage of the slime deposition up to fill is continuously monitors storage activity.

As a result, slime deposition must be subject to the process of ecological closure. The ecological closure of slime deposition will run according to specific projects.

Table 2

Concentrations of chemical elements in P1 - levigation test L/S = 10l/kg and P2 - C (0) - first eluate of percolation test L/S = 0.1 l/kg)

Indicator	Values obtained		Values maximum allowed Order 95/2005	
	P1 - L/S = 10 l/kg mg/kg s.u	P2- C(0), mg/l	L/S = 10 l/kg mg/kg s.u	C(0) mg/l
pH	9.03	8.22		
HCO_3^{2-}	60	-		
HCO_3^-	1100	64		
Cl^-	1880	113	25000	15000
SO_4^{2-}	18050	1045	50000	17000
NO_3^-**	11070	487		
Ca^{2+}	12000	700		
Mg^{2+}	68.8	5.7		
Na^+	2260	162		
K^+	410	29		
F^-	7.3	0.5	500	120
Cu	0.42	0.02	100	60
Ni	2.0	0.15	40	12
Zn	2.3	0.14	200	60
Cd	0.16	0.003	5	1.7
Cr, total	42.5	1.92	70	15
Mn	0.45	0.03	-	-
Pb	1.7	0.10	50	15
Co	2.5	0.22		
Fe	13.7	0.8		

CONCLUSIONS

1. Slime resulted of the technological process of pickling steel bands in S.C. OȚEL INOX S.A. Târgovişte was stored in depositions located inside the company. Slime is a metal waste which cannot be recuperated, and its storage in the deposition is final.
2. From the chemical point of view, slime is a mixture of oxides and hydroxides of heavy metals. The reaction of the slime samples were moderately alkaline, strongly alkaline and extremely alkaline.
3. The slime presented a strong salinization, mainly sulphatic and the dominant salts are calcium sulfate, calcium nitrate, sodium nitrate and calcium chloride.
4. Because of the chemical elements determined in slime samples had generally similar values in the surface horizons and the profile, show that slime have a similar composition.
5. In the levigation test and first eluate of the percolation test calcium salts predominate, followed by sodium salts and the content of heavy metals in the levigation sample is low. The P1 reaction is moderately alkaline and P2 reaction is slightly alkaline.
6. The analytical values determined for all the elements are within the range given by the *Order 95/2005* and there is no danger of water pollution with those chemical elements.
7. Slime is stored in a concrete pit which is a barrier for soluble salts and heavy metals to infiltration into the soil and underground water.
8. Slime deposition no. 3 stored in the S.C. OȚEL INOX S.A. area containing pickling process slime can be subject to ecological closure, in accordance with the environmental legislation.

REFERENCES

1. Lăcătuşu R., Nineta Rizea, Rodica Lazăr, Beatrice Kovacsovics, Mihaela Lungu, 2005. *Bilanț de mediu nivel II la depozitul de şlam din incinta unității S.C. OȚEL INOX S.A. Târgovişte*. Arhiva ICPA.
2. ***MMGA, Ordin nr. 95/12.02.2005 privind stabilirea criteriilor de acceptare şi procedurilor preliminarede acceptare a deşeurilor la depozitare şi lista națională de deşeuri aceptate în fiecare clasă de depozit de deşeuri, Monitorul Oficial al României, Partea I, Nr. 194/08.03.2005.
3. ***ICPA, 1981. *Metodologia de analiză agrochimică a solurilor în vederea stabilirii necesarului de amendamente şi îngrăşăminte*. Vol. I. Metode, rapoarte, îndrumări, nr. 18, Redacția de propagandă tehnică agricolă, Bucureşti.