

HORMITE GROUP EVALUATION FOR ITS USE ON THE TECHNOLOGY OF RESIDUES DISPOSAL

Wilma de Carvalho Pereira
ENSP/FIOCRUZ, Rua Leopoldo Bulhões, 1480
E-mail: carvalho@ensp.fiocruz.br

Dalton Marcondes Silva
ENSP/FIOCRUZ

Juremi Oliveira Carvalho
ENSP/FIOCRUZ

Nelson Moura Brasil do Amaral Sobrinho
Departamento de Agronomia/UFRRJ

Roberto Cerrini Villas Boas
CETEM/MCT

RESUMO

O presente trabalho tem como objetivo o estudo dos elementos potencialmente contaminantes presentes nos rejeitos industriais que são dispostos no meio ambiente. Tem como meta o conhecimento dos parâmetros necessários para o controle da mobilidade destes metais presentes nos resíduos. Dois tipos de resíduos foram estudados: o primeiro proveniente da indústria de galvanoplastia (Classe I: ABNT, 1987); e o outro proveniente da indústria de produção de aço (escória da aciaria). Este último rejeito é considerado relativamente estável pelos padrões vigentes devido às suas características (Cd<0.5 mg/Kg, Pb<10 mg/Kg, Co<5 mg/Kg, Cu=61 mg/Kg, Cr=280 mg/Kg, Ni<1.5 mg/Kg, Zn=75 mg/Kg). No entanto, até o momento, não existe uma alternativa para a sua total utilização. Foram realizados testes experimentais de disposição em células de acrílico, utilizando água acidificada para simular precipitação pluviométrica de regiões industrializadas. No final do processo foi observado uma capa impermeável com um aspecto cristalino formada entre os resíduos da Ingá e CSN. A melhor forma foi obtida com a seguinte disposição (do topo à base): resíduo da Ingá, escória de aciaria e argilomineral.

PALAVRAS-CHAVE: Disposição; minerais de argila; resíduos industriais

ABSTRACT

The purpose of this work is to study the potentially contaminating trace elements present in industrial waste that is discharged into the environment. The aim was to assess the parameters needed for it to be used in controlling the mobility of the potentially contaminating trace elements present in the residues. Two types of waste were studied: a waste from the electroplating industry (Class I: ABNT, 1987), and refuse slag from Cia Siderúrgica Nacional – CSN). Even though this waste is considered relatively stable within the established standards set by current legislation due to its characteristics (Cd<0.5 mg/Kg, Pb<10 mg/Kg, Co<5 mg/Kg, Cu=61 mg/Kg, Cr=280 mg/Kg, Ni<1.5 mg/Kg, Zn=75 mg/Kg), there is so far no feasible alternative for its total reutilization. Bench-scale tests were performed whereby an acidified liquid to simulate the rainfall typical in highly industrialized regions was introduced in the cells that contained layers of the waste, steelworks slag and clay minerals under study. At the end of the process it was noted that a layer impermeable with a crystalline appearance was formed between the Ingá and CSN residues. The better form of disposal, so far, was materials layered in the following order (from top down): Ingá, steelworks residues and clay mineral.

KEY-WORDS: Disposal; clays minerals; industrial residues.

1. INTRODUCTION

This work is based on a study of the characteristics, properties and availability of the clay in an alkaline waste from the steel industry (steelworks slag). The aim was to assess the parameters needed for it to be used in controlling the mobility of the potentially contaminating trace elements present in the liquid effluent that percolates out of acid waste. The development of a process for disposing of such waste was studied in this work. Two types of waste were analyzed: an acid one from Cia. Ingá, ($Zn = 22294,4 \text{ mg Kg}^{-1}$, $Cd=175,2 \text{ mg Kg}^{-1}$, $Pb=2486,8 \text{ mg Kg}^{-1}$, $Cu=123,2 \text{ mg Kg}^{-1}$, $Ni=32,0 \text{ mg Kg}^{-1}$), and an alkaline one, figure 1 (slag from the Cia Siderúrgica Nacional – CSN steelworks).

Clay minerals was studied with a view to its being used to absorb potentially contaminating elements. The hormite group has received considerable study due to its characteristics, which include: (a) its cation exchange versatility, which allows a large variety of cations to be introduced in its layers; (b) its capacity to swell up, which allows molecules of different sizes to fit between its layers; and (c) its capacity to exfoliate and alter its arrangement without changing the crystal structure of its layers. The hormite group comprises atapulgite and sepiolite minerals.

The mobility of potentially toxic trace elements is of great importance given certain factors, such as the soil (overwhelmingly acid soils in Rio de Janeiro) and the climate (high rainfall rate) characteristic of this tropical region. Alkaline waste produced by the steel industry is currently a considerable environmental liability. Though such waste is considered stable in existing legislation, given its characteristics ($Cd < 0.5 \text{ mg Kg}^{-1}$, $Pb < 10 \text{ mg Kg}^{-1}$, $Co < 5 \text{ mg Kg}^{-1}$, $Cu=61 \text{ mg Kg}^{-1}$, $Cr=280 \text{ mg Kg}^{-1}$, $Mo < 10 \text{ mg Kg}^{-1}$, $Ni < 1.5 \text{ mg Kg}^{-1}$, $Se < 3.0 \text{ mg Kg}^{-1}$, $Zn=75 \text{ mg Kg}^{-1}$), there is as yet no viable production-scale option for its total reuse. This being the case, if such waste were used as an alkanizing agent together with clay, forming 2:1 layer structures in sanitary and industrial landfills, this could provide a satisfactory and feasible final disposal for it (in ecological and economic terms).

2. METHODOLOGY

2.1 Sampling and analytical methods

The waste matter was collected randomly then homogenized, quartered and split into approximately 1kg fractions. All the material was analyzed using a permeameter to find its hydraulic conductivity, according to Darcy's law ($q = -K (\Delta\Psi_B - \Delta\Psi_A) / \Delta Z$). Plasticity limit tests were performed using the standard method set out in NBR -7180. A mineralogical analysis was made using a diffractometer (Siemens AXS, D8). An additional test was made using an x-ray fluorescence technique (Phillips, I model TW2400). The trace elements in all the material (waste matter and clay) and the percolate were analyzed by atomic absorption spectrometry (Spectr AA - 600 VARIAN - acetylene gas used – manual operation – hollow cathode lamps – photron lamps).

2.2 Experimental design

Bench-scale tests were performed whereby an acidified liquid influent flowed through transparent acrylic cells. The cells contained layers of the waste under study, the material being used as an absorbent and grains of quartz, which were non-reactive in the process (forming the base) so that the material would be retained within the cell without it becoming blocked. The liquid introduced was intended to simulate the rainfall typical in highly industrialized regions (metalworks, steelworks, power plants, etc.), so it was acidified with sulfuric acid to pH 4 to 4.5. The liquid effluent was collected in plastic bottles and analyzed in atomic adsorption equipment. The schematic design of the experimental design is shown in Figure 1.

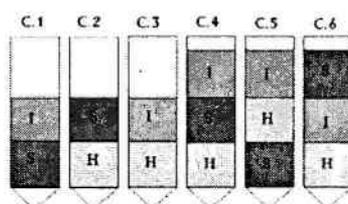


Figure 1. Schematic diagram of the experimental design showing the layers in the cells: waste from Ingá, clay (hormite) and steelwork slag from CSN.

3. RESULTS AND DISCUSSION

The composition of the materials was obtained using x-ray fluorescence to determine the relative content of different compounds. Table I below shows the mineral compounds common to both the materials investigated.

The mineral composition of the clay obtained through x-ray diffractometry can be seen in Figure 3. We can see the base spectra from the atapulgitite, sepiolite and kaolinite group. The diffractogram also points to the presence of mixed irregular and inter-stratified layers of illite and montmorillonite, as well as small proportions of quartz.

The results of the hydraulic conductivity analyses of the material can be seen in Table II. The results from the analyses of the liquids collected in the experiment can be seen in Table III.

Once the experiment was started, it took three days for the liquid to start dripping through, and it was approximately 34 days after this that the experiment was stopped. Figure 2 shows the experimental setup in the laboratory at Universidade Federal Rural do Rio de Janeiro. At the end of the experiment a cementation was observed at the interface of the waste from CSN and Ingá, which blocked the flow of the liquid being introduced at the top, as can be seen in Figure 3. Though the solidification process was slower in other cells containing waste from CSN, a decision was taken to interrupt the process, since the flow rate had fallen in all the cells and the quantity of material already collected was already enough for an evaluation to be made.

Table I. Results of the x-ray fluorescence analysis (%).

	Hormite group
MgO	6.6
Al ₂ O ₃	13.5
SiO ₂	66.6
TiO ₂	0.64
MnO ₂	0.62
Fe ₂ O ₃	4.4

Table II. Results of atomic absorption spectrometry for elements concentrations. (mg/Kg)

	<i>Fe</i>	<i>Pb</i>	<i>Cd</i>	<i>Cu</i>	<i>Mn</i>	<i>Zn</i>
Ingá	103.8	3199	665.2	57.65	2791	1573
CSN	143.1	< 10	< 0,5	61	18125	75
Hormite	25.11	63	32.21	19.67	1805	6.96

The Cd, Cd, Cu and Zn value was obtained from the steel industry CSN. The results of the analysis of trace metals present in the material used in the simulation process are presented in chart form in Figure 5.

The hydraulic conductivity value was obtained from a permeameter with a constant head of water. The results are shown in Table III.

Table III. Results of the hydraulic conductivity tests on the materials.

Material	Hydraulic conductivity (cm/s)
Ingá	2.19×10^{-4}
CSN	10^{-2}
Hormite group	4.2×10^{-3} cm/s

The cells 1, 2 and 3 may be observed on table IV and show the four runs (a, b, c and d) because they do not present retention. The cells 4, 5 and 6 are also represented by graphics for a better visualization of the process results with the three studied materials.

The results of the liquid effluents from cell are 4, 5 and 6 shown in table IV and figures 2 to 4.

Table IV. Metal concentrations in the liquids collected in the tests

Cell	Cd	Fe	Cu	Pb	Mn	Zn
Cell 1						
a	13.26	2.48	0.10	0.69	58.42	3312.45
b	16.86	3.44	ND	0.86	48.68	2328.15
c	16.67	4.07	ND	0.55	24.30	448.8
d	2.42	0.85	ND	0.16	0.08	24.2
Cell 2						
a	3.48	0.41	ND	0.04	ND	11.9
b	7.58	1.53	ND	0.11	ND	4.3
c	12.91	2.95	ND	0.18	ND	
d	1.30	ND	ND	ND	0.12	13.2
Cell 3						
a	6.70	2.03	0.02	0.72	14.84	1348.95
b	11.90	1.79	ND	0.77	18.47	905.25
c	19.18	4.82	ND	1.11	28.34	1866.6
d	7.25	1.26	0.05	0.99	32.00	1428.00
Cell 4						
b	11.24	2.95	ND	0.39	10.23	295.8
c	11.12	3.03	ND	0.45	9.86	155.55
d	3.38	0.70	ND	0.39	7.73	89.25
Cell 5						
b	14.19	3.54	ND	0.48	16.92	525.3
c	0.48	0.13	0.01	0.15	ND	2.35
d	2.11	0.98	ND	0.21	ND	ND
Cell 6						
b	12.82	3.38	ND	0.35	8.68	22.95
c	11.15	2.44	0.05	0.78	53.97	2697.9
d	10.52	2.19	0.01	0.59	44.38	2223.6

ND – not detected

Identification model, where:

a = 1st run

b = 2nd run

c = 3rd run.

d = 4rd run

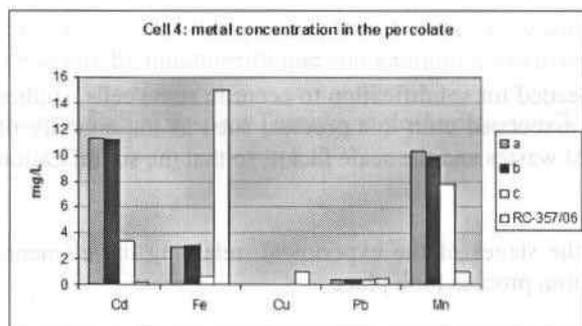


Figure 2. Results of the metal concentrations after percolation through cell 4, with the materials layered in the following order (from top down): Ingá residues, steelworks waste and clay.

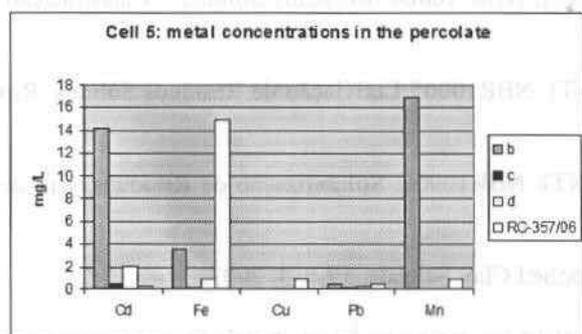


Figure 3. Results of the metal concentrations after percolation through cell 5, with the materials layered in the following order (from top down): Ingá waste, clay and steelworks waste.

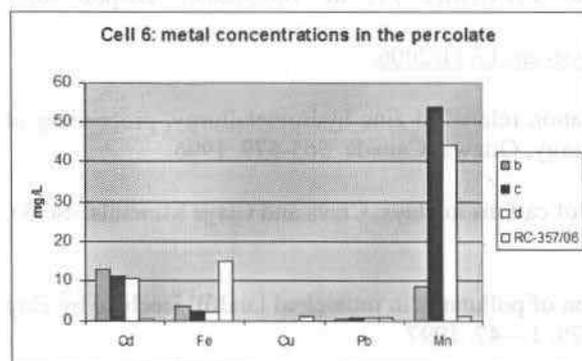


Figure 4. Results of the metal concentrations after percolation through cell 6, with the materials layered in the following order (from top down): steelworks waste, Ingá waste and clay.

In cell 4, 5 and 6 a solidification process occurred that made it impermeable. At the end of the process it was noted that a layer with a crystalline appearance had been formed, as mentioned above. The clay helped retain the liquid within the upper layer (CSN waste), probably because of its saturation capacity and low permeability, which meant the solidification progressed more quickly than in the other cells.

4. CONCLUSIONS

The retention of the metals under study must be associated to cation exchange and the formation of insoluble salts. The clay seems to have helped the retention of cadmium: in cell 3 even in an acid medium, this element was retained to a significant extent, while in cell 1, which contained no clay, only an insignificant amount was retained.

The layer of impermeable material that was formed between the Ingá and CSN waste may contribute positively towards the disposal of the waste under study. This layer may be used as an impermeable layer, which could have

Wilma de Carvalho Pereira, Dalton Marcondes Silva, Juremi Oliveira Carvalho, Nelson Moura Brasil do Amaral Sobrinho, Roberto Cerrini Villas Boas.

applications in sanitary landfills. Though we controlled the time needed for solidification to occur in some cells, studies still need to be made into the influence of the other parameters associated with this process, such as the quantity of water, the temperature, the thickness of the layers, the proportion of wastes and the scale factor, so that the solidification process can be better understood.

Finally, cell 4 showed excellent results throughout all the stages of the experiment, retaining the elements under study in compliance with all legislation before the solidification process took place.

5. REFERENCES

- ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (ABNT). NBR 10004. Resíduos Sólidos – Classificação. Rio de Janeiro. 1987.
- ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (ABNT). NBR10005 Lixiviação de Resíduos Sólidos. Rio de Janeiro. 1987.
- ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (ABNT). NBR10006. Solubilização de Resíduos. Rio de Janeiro. 1987.
- Bergava, F. & Lagaly G. Surface modification of clay minerals. *Applied Clay Science*, 19, 1-3. 2001.
- Brewster M.D. & Passmore R.J. Use of electrochemical ion generation for removing heavy metals from contaminated groundwater, *Environmental Progress* 13 (2), pp. 143–148. Abstract-Elsevier BIOBASE | Abstract + References in Scopus | Cited By in Scopus. 1994.
- CONSELHO NACIONAL DE MEIO AMBIENTE. Resolução CONAMA 357 de 18/03/2005. Dispõe sobre classificação das águas. Disponível em <http://www.mma.gov.br/port/conama/res/res86/res2086.html>. Acesso em 17/11/2006.
- Farfán J.L.V. Bentonites as a material for a controlling contamination related to zinc hydrometallurgy, proceeding of the second international symposium on iron control in hydrometallurgy, Ottawa, Canadá. 565-579. 1996.
- Fitch, A.; Song J.; Stein J. Molecular structure effects on diffusion of cations in clays. *Clays and Clays Minerals*. 44 (3), 370-380. 1996.
- Griffin, R. A.; Frost R. R.; Robinson G.D.; Shimp, N.F. Attenuation of pollutants in municipal landfill leachate by clay minerals: Heavy metal adsorption, *Environmental Geology Notes*, 79, 1 – 47. 1997.
- Nascimento S.C.; Hypolito R.; Ribeiro A.A. Disponibilidade de metais pesados em aterro de indústria siderúrgica. *Revista de Engenharia Sanitária e Ambiental*. 11 (3). 2006.
- Oliveira M.R.C. & Martins J. Caracterização e classificação do resíduo sólido "pó do balão", gerado na indústria siderúrgica não integrada a carvão vegetal:- estudo de um caso na região de Sete Lagoas/MG. *Química Nova* vol.26 (1). 2003.
- Pinheiro, R.S. Inertização de resíduo perigoso através do uso de resíduos industriais alcalinos. Tese de Mestrado. Instituto de Agronomia, Universidade Federal Rural do Rio de Janeiro, Brazil. 74 p. 2003.
- Rebhun M. & Galil N. Wastewater treatment technologies. In: L. Zirm and J. Mayer, Editors, *The Management of Hazardous Substances in the Environment*, Elsevier Applied Science, London, New York. pp. 85–102. 1990.
- Rocca, A. A. C et al. Resíduos Sólidos Industriais, CETESB: São Paulo, 234 p. 1993.
- STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER. 20th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA. 1998

Srivastava S.K.; Renu Tyagi, Pant N.; Pal N.. Studies on remove of some toxic metal ion part II (removal of lead and cadmium by montmorillonite and kaolinite). *Environmental Technology Letters*, 10: 275 - 282. 1989.

Santos, P. S. *Ciência e Tecnologia de Argilas*, vol. 3, EDGARD BLUCHER, São Paulo. 1992.