ENVIRONMENTAL BEHAVIOR OF SOILS AND MIXTURES OF SOIL-WHITEWASH MUD[1]

Carlos Cardoso Machado[2], José Maurício Machado Pires[3], Maurício Paulo F. Fontes[2], Reginaldo Sérgio Pereira[4], Carla Ribeiro Machado e Portugal[5]

ABSTRACT - The present study sought to observe the behavior of soils in natural state and in mixtures, in different ratios, with the industrial solid residue called whitewash mud. The work was conducted with samples of typical soils from the region of Alagoinhas, Bahia–Brazil. Wet chemical analysis and atomic absorption spectrophotometry were used in order to obtain the classification of the industrial solid residue. Solubilization and leaching tests were performed and X-ray diffraction and electron microscopy techniques were carried out. The results showed that the whitewash mud was classified as non-inert, but with great capacity of heavy metal retention largely owed to the kaolinite and goethite presence in the clay fraction of the soils, making it difficult to have heavy metals readily available for exchange.

Key words: Soils, industrial solid residue, whitewash mud, environmental problem.

COMPORTAMENTO AMBIENTAL DE SOLOS E MISTURAS SOLO LAMA-DE-CAL

RESUMO - O presente estudo buscou observar o comportamento de solos em seu estado natural e em misturas, em diferentes teores, com o resíduo sólido industrial denominado lama-de-cal. A pesquisa foi conduzida com amostras de solos típicas da região de Alagoinhas, Bahia-Brasil. A análise química por via úmida e espectrofotometria de absorção atômica foram usadas para obter a classificação do resíduo sólido industrial. Testes de solubilização, lixiviação, analise de raios X e microscopia eletrônica de varredura foram executados. Os resultados indicaram que a lama-de-cal não é inerte, mas com grande capacidade de retenção de metais pesados, em grande parte devido à presença de caulinita e goethita na fração argila dos solos.

Palavras-chave: Solos, resíduo sólido industrial, lama-de-cal, comportamento ambiental

1. INTRODUCTION

The terms pollution and contamination are being heavily used in the current days. For Crathorne et al. (1996), they are mistakenly taken as synonymous in the everyday common language usage. In the scientific field they have different meanings. The term contamination is used to designate a chemical substance in a sample without evidence that it causes problems. The term pollution is used in cases where the presence of the substance is harmful. Pollutants are therefore chemical substances that cause damage to the environment. There are several types of pollution, going from the simple thermal pollution to the input of heavy metals in the environment.

Industrial waste is one of the main responsible factors for environmental pollution, being originated

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[2]Federal University of Viçosa, Professor-Viçosa, MG, Brazil-machado@.ufv.br mpfontes@mail.ufv.br
[3]Federal University of Viçosa, Graduate Student-Viçosa, MG, Brazil- jmauricio@uaimail.com.br;
[4]Federal University of Viçosa, Graduate Student- Viçosa, MG, Brazil- rpereira@buynet.com.br
[5]Federal University of Uberlândia, Graduate Student - Uberlândia, MG, Brazil

from cooling processes, washing, discharges, extractions, impregnations, chemical treatments, among others. It is one of the great concerns nationally and worldwide (ROCCA et al., 1993).

The reuse of industrial by-products represents one of the technological alternatives for application for those residues. Works with that focus are being developed in laboratories of the Federal University of Viçosa, MG, (UFV), where the utilization of some of these residues in pavements of forest highways is sought. Particularly one residue with great potential for reutilization is whitewash mud, coming from the cellulose and paper industry. Thus, the environmental aspect of its utilization becomes of fundamental relevance.

The present study has therefore the following objectives: (a) to characterize chemically and mineralogically the industrial solid residue called whitewash mud; (b) to carry through the classification of this material as related to its environmental potential danger when used together with soil samples.

2. MATERIAL AND METHODS

2.1. Samples of soils

Two samples of soils, coming from Klabin-Bacell company, Alagoinhas, Bahia - Brazil, were used in the study. The samples were identified as:

* Farm Klabin Bacell – Sand Soil (SS);
* Farm Klabin Bacell – Gravel Soil (GS);

2.2. Industrial solid residue or whitewash mud

The solid residue whitewash mud derived from paper and cellulose processing was used in this study. Residue particle size of 0.25 mm sieve was used.

2.3. Dosage of the mixtures soil + whitewash mud

The amounts of whitewash mud were: 5, 10, 15, 20 and 25% of soil dry weight.

2.4. Laboratory Testing Program

The laboratory tests with the soil samples in natural state and in mixtures with the whitewash mud consisted of the following: determination of the trace elements Cu, Cd, Cr, Fe, Pb, Zn and Mn by atomic absorption spectrophotometry (ABNT, 1987a - NBR 10004); (b) soil classification of: leaching test by determination of Cd, Cr and Pb (ABNT, 1987b–NBR 10005), solubilization test by determining the contents of Cr, Pb, Cd, Fe, Mn and Na (ABNT, 1987c–NBR 10006); (c) textural analysis and cation exchange capacity (EMBRAPA, 1990); (d) determination of the organic carbon content (WALKLEY, 1947); and (e) X-ray diffraction for determination of clay fraction minerals (FORMOSO, 1984).

3. RESULTS AND DISCUSSION

3.1. Determination of trace elements

The determination of trace elements present in the soil samples and in the mixtures soil-whitewash mud was performed according to Standards 10004 of ABNT (ABNT, 1987a). The results of the soil samples and the mixtures soil-whitewash mud are shown in Tables 1 and 2.

Table 1 shows the presence of iron, zinc and manganese in the Sand and Gravel Soil samples. A larger concentration of iron, zinc and manganese was observed in the Sand Soil samples.

Table 2 shows that the concentration of the elements copper, iron, zinc and manganese decreased with the increasing the concentration of whitewash mud in the gravel soil mixtures, but it increased in sandy soil mixtures.

3.2. Soils classification in relation to the degree of pollution

Soil classification in relation to the pollution level was carried out according to the ABNT's Standards 10005 and 10006 (ABNT, 1987b,c).

Table 1 - Amount of trace elements of natural soil samples (mg/g)
Tabela 1 - *Quantidade de elementos traços em amostras de solo natural (mg/g)*

Samples	Cu	Cd	Cr	Fe	Pb	Zn	Mn
SS_1	ND	ND	ND	18065	ND	72.8	48.5
SS_2	ND	ND	ND	3207	ND	70.3	19.4
SS_3	ND	ND	ND	15219	ND	65.9	37.2
(subsamples)							
GS_1	100	ND	ND	10500	ND	20.3	7.8
GS_2	125	ND	ND	12000	ND	18.7	10.5
GS_3	142	ND	ND	7250	ND	15.2	9.6

ND = Not detected
SS_1, SS_2 and SS_3 are subsamples of the *sand soil* samples. GS_1 GS_2 and GS_3 are subsamples of the *gravel soil* samples.

Table 2- Amount of trace elements in the mixtures of soil-whitewash mud (μg/g)
Tabela 2 *- Quantidade de elementos traços em amostras de misturas solo-lama-de-cal (μg/g)*

Samples	Cu	Cd	Cr	Fe	Pb	Zn	Mn
SS_1 + 10% whitewash mud	ND	ND	5.1	1095.6	ND	16.8	ND
SS_2 + 10% whitewash mud	ND	ND	22	1067.2	ND	26	ND
SS_1 + 15% whitewash mud	ND	ND	20	1615	ND	26.7	ND
SS_2 + 15% whitewash mud	ND	ND	2.3	1485.8	2.2	29	11.5
SS_1 + 20% whitewash mud	ND	ND	18.2	1247.3	ND	18.2	56.5
SS_2 + 20% whitewash mud	ND	ND	25.4	1349.6	428.2	40.3	52.2
SS_1 + 25% whitewash mud	ND	ND	22.4	1309.6	428.2	40.3	52.2
SS_2 + 25% whitewash mud	ND	ND	22.3	1300	442.4	40.1	57.0
GS_1 + 10% whitewash mud	201.4	1.8	106	15887.8	23.9	99.2	89.5
GS_2 + 10% whitewash mud	254	2.2	123	16792.3	33.1	116	96.8
GS_1 + 15% whitewash mud	419	6.9	44	11317.5	62.3	100.2	49.6
GS_2 + 15% whitewash mud	419	6.9	44	11317.5	62.3	100.2	49.6
GS_1 + 20% whitewash mud	67.3	ND	ND	4677.8	ND	9.6	5.7
GS_2 + 20% whitewash mud	67.3	ND	ND	4677.8	ND	9.6	5.7
GS_1+ 25% whitewash mud	67.3	ND	ND	4677.8	ND	9.6	5.7
GS_2 + 25% whitewash mud	67.3	ND	ND	4677.8	ND	9.6	5.7

For both situations it was noticed that some elements were below the detection limit (ND).

3.2.1. Results of the leaching tests

Table 3 shows the results of the leaching tests with soil samples and mixtures of soil-whitewash mud.

3.2.2. Results of the solubilization tests

Table 4 shows the results of the solubilization tests with soil samples and soil- whitewash mud.

Tables 3 and 4 present the contents of several trace elements, including sodium, obtained in the leaching and solubilization tests. The simple inspection and comparison of the values obtained in relation to the values controlled by Standard 10004 of ABNT (Tables 5 and 6) suggest that the whitewash mud can be classified as a non-inert material because of the sodium high concentration found in these tests.

Table 3 – Contents of Cd, Cr and Pb in μg/mL in soil and mixture leaching tests
Tabela 3 *– Conteúdos de Cd, Cr e Pb (μg/mL) nos ensaios de lixiviação de solos e misturas de solo-lama-de-cal*

Samples	Cd	Cr	Pb
SS	< 0.5	<5.0	<5.0
GS	< 0.5	<5.0	<5.0

a) natural soil

samples	Cd	Cr	Pb
SS+ 10% whitewash mud	< 0.5	<5.0	<5.0
SS + 15% whitewash mud	< 0.5	<5.0	<5.0
SS + 20% whitewash mud	< 0.5	<5.0	<5.0
SS + 25% whitewash mud	< 0.5	<5.0	<5.0
GS + 10% whitewash mud	< 0.5	<5.0	<5.0
GS + 15% whitewash mud	< 0.5	<5.0	<5.0
GS + 20% whitewash mud	< 0.5	<5.0	<5.0
GS + 25% whitewash mud	< 0.5	<5.0	<5.0

b) mixture of soil- whitewash mud

Table 4 - Contents of Cd, Cr, Pb, Mn, Fe and Na (μg/mL), in the solubilization test
***Tabela 4** - Conteúdo de Cd, Cr, Pb, Mn, Fe e Na (μg/mL) nos ensaios de solubilização de solos e misturas de solo-lama-de-cal*

Samples	Cd	Cr	Pb	Mn	Fe	Na
SS_1	< 0.005	<0.05	<0,.5	<0.1	< 0.3	1866
SS_2	< 0.005	<0.05	<0.05	<0.1	< 0.3	1316
GS_1	< 0.005	<0.05	<0.05	<0.1	< 0.3	1316
GS_2	< 0.005	<0.05	<0.05	<0.1	< 0.3	1316
Mean	< 0.005	<0.05	<0.05	<0.1	< 0.3	1453

a) natural soil

Samples	Cd	Cr	Pb	Mn	Fe	Na
SS_1 + 10% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	4500
SS_2 + 10% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	5000
SS_1 + 15% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	4000
SS_2 + 15% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	5500
SS_1 + 20% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	5500
SS_2 + 20% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	4050
SS_1 + 25% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	5000
SS_2 + 25% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	4500
GS_1 + 10% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	7000
GS_2 + 10% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	6000
GS_1 + 15% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	4000
GS_2 + 15% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	4000
GS_1 + 20% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	5000
GS_2 + 20% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	6000
GS_1 + 25% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	6000
GS_2 + 25% wwash mud	< 0.005	<0.05	<0.05	<0.1	< 0.3	6200
Mean	< 0.005	<0.05	<0.05	<0.1	< 0.3	5196

b) mixtures of soil- whitewash mud

Table 5 - Maximum allowable values in the extract from the leaching tests
***Tabela 5** - Valores máximos permissíveis no extrato dos ensaios de lixiviação*

Pollutant	Maximum limit (μg/mL)
Cd	0.5
Pb	5.0
Cr	5.0

Table 6 - Maximum allowable values in the extract from the solubilization tests
***Tabela 6** - Valores máximos permissíveis no extrato dos ensaios de solubilização*

Pollutant	Maximum limit (μg/mL)
Cd	0.005
Pb	0.05
Cr	0.05
Fe	0.3
Mn	0.1
Na	200

3.3. Results of the textural analysis of soils and mixtures of soil-whitewash mud

Table 7 presents a synthesis of the main results for the textural analysis of natural soil and mixtures soil-whitewash mud in different concentrations.

Table 7 - Results for the textural analysis of soils and mixtures of soil-mud of whitewash
***Tabela 7** - Resultados da análise textural de solos e misturas solo-lama-de-cal*

Samples	%Coarse sand	%Fine sand	%Silt	%Clay	Textural class
S	65	12	5	18	Sandy loam
SS	27	67	3	3	Sand
SS + 20% whitewash mud	12	72	14	2	Loamy sand
SS + 10% whitewash mud	14	75	7	4	Sand
SS + 15% whitewash mud	5	53	22	20	Sandy loam
GS + 10% whitewash mud	8	63	12	17	Sandy loam
GS + 25% whitewash mud	9	56	18	17	Sandy loam
GS + 15% whitewash mud	8	58	16	18	Sandy loam
GS + 20% whitewash mud	9	78	10	3	Sand

3.4. Analysis of X-Ray diffraction

Table 8 shows the main results of soil samples and mixtures of soil-whitewash mud X-Ray analysis. In general, kaolinite, goethite, gibbsite and quartz were the main minerals found.

3.5. Results of Cation Exchange Capacity (CEC)

Table 9 presents the results for cation exchange capacity (CEC) of the samples of natural soil the mixture soil-whitewash mud. The importance of this analysis is that it gives a pretty good idea of the capacity for adsorption on the surface of the mineral components of these soils and the soil mixtures. It can be noticed that the whitewash mud increases soil sample CEC making the mixtures much better cation adsorbent.

Table 8 - Results of X-ray diffraction analysis
Tabela 8 - *Resultados de analises de difração de raios X de solos e misturas solo-lama-de-cal*

Samples	Mineralogy
GS	Kt; Gb; Go
SS	Kt; Go; Qz
SS + 20% whitewash mud	Kt; Gb; Go
SS + 10% whitewash mud	Kt; Gb
SS + 15% whitewash mud	Kt; Qz
GS + 10% whitewash mud	Kt; Gb; Go
GS + 25% whitewash mud	Kt; Gb; Go
GS + 15% whitewash mud	Kt; Gb; Go
GS + 20% whitewash mud	Kt; Qz

Table 9 - Cation exchange capacity of soil and soil mixtures
Tabela 9 - *Capacidade de troca catiônica de solos e misturas solo-lama-de-cal*

Samples	CEC (Cmolc/kg)
SS	6.0
GS	4.0
GS + 25% whitewash mud	27.0
GS + 20% whitewash mud	41.0
GS + 15% whitewash mud	29.0
GS + 10% whitewash mud	24.0
SS + 25% whitewash mud	41.0
SS + 20% whitewash mud	39.0
SS + 15% whitewash mud	33.0
SS + 10% whitewash mud	20.0

3.6. Results of organic carbon analyses

Table 10 shows that the contents of organic carbon are very low, showing a very poor relationship between these sandy soils and mixtures soil- whitewash mud and organic carbon. Sand and organic carbon can not form stable complexes as compared to soils with larger contents of clay fraction.

Table 10 - Results of organic carbon contents in %
Tabela 10 - *Resultados do teor de carbono orgânico (%) de solos e misturas solo-lama-de-cal*

Samples	% OC
GS	0.07
GS + 10% whitewash mud	0.4
GS + 15% whitewash mud	0.4
GS + 20% whitewash mud	1.0
GS + 25% whitewash mud	0.4
SS	0.4
SS + 10% whitewash mud	0.4
SS + 15% whitewash mud	0.5
SS + 20% whitewash mud	0.4
SS + 25% whitewash mud	0.3

4. CONCLUSIONS

a) The mixture soil- whitewash mud was not a dangerous material as far as the pollution point of view is concerned;

b)The contents of Cadmium, Chromium and Lead in the mixture soil-whitewash mud were below the limits recommended by the Brazilian Association of Technical Standards (ABNT);

c) The whitewash mud belongs the Class 2 of ABNT, therefore the material is not inert, due to the contents of Sodium obtained in the solubilization tests, which are above the limit recommended by ABNT Standards;

d) The contents of kaolinite and goethite ranged from 20 to 50%, imparting to these natural soils and the mixtures soil-whitewash mud a good capacity to retain heavy metals, making them less available to exchange and percolation to the water system;

e) Natural soils and the mixtures soil-whitewash mud presented low contents of organic carbon showing that their sandier nature does not allow them to hold higher amounts of organic carbon.

5. REFERENCES

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT: **NBR 10004** – Classificação de resíduos sólidos. [BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS– NBR 10004. Classification of solid residues]. Rio de Janeiro: ABNT, 1987a. 63 p.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT: **NBR 10005** – Lixiviação de resíduos sólidos. [BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS–NBR 10005. Leaching of solid residues]. Rio de Janeiro: 1987b. 7 p.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT: **NBR 10006** – Solubilização de resíduos sólidos. [BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS– NBR 10006. Solubilization of solid residues]. Rio de Janeiro: 1987c. 2 p.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT: **NBR 10007** – Amostragem de resíduos sólidos. [BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS– NBR 10007. Sampling of solid residues]. Rio de Janeiro: 1987d. 25 p.

CRATHORNE, B.; DOBBS, A. J.; REES, Y. Chemical pollution of aquatic environment by priority pollutants and its control. In: HARRISON R. M. (Ed.). **Pollution causes, effects and control**. 3. ed. England: The Royal Society of Chemistry, 1996. p.1.

FORMOSO, M. L. L. **Difratometria de raios-X**. In: SANTOS, P. S. (Coord.). Técnicas analíticas instrumentais aplicadas à geologia. São Paulo: Edgard Blücher, 1984. 218 p.

MANUAL DA EMBRAPA. Rio de Janeiro: EMBRAPA: 1990. 470 p.

ROCCA, A. C. C.; LACOVONE, A. M. M. B.; BARROTTI, A. J. **Resíduos sólidos industriais.** 2. ed. São Paulo: CETESB, 1993.

WALKLEY, A. A critical examination of a rapid method for determining organic carbon in soils: effect of variations in digestion conditions and of inorganic soils constituents. **Soil Science**, n. 63, p. 251-263, 1947.