

"Inertization and promotion of Prestige fuel oil spill doughy residues recycling"



2.Binary mixtures. (Chemical aspects).

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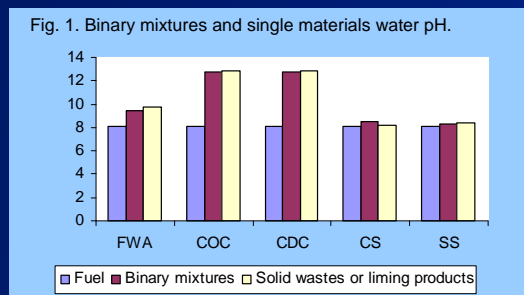
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Introduction

Some of the best binary mixtures (from the physical point of view) previously obtained, including fuel oil and several solid industrial wastes or liming products, were chemically analyzed as were the single materials. Marine environment added a high water and soluble salts content to the Prestige fuel oil after the spill, and degrading hydrocarbons process diminished carbon content referred to fresh fuel (Le Cedre, 2002). Fly wood ash and partially dehydrated industrial slurries (slate and CaCO₃ rich slurry) are very heterogeneous materials with physical and chemical properties depending of multiple factors and varying for each material remittance.

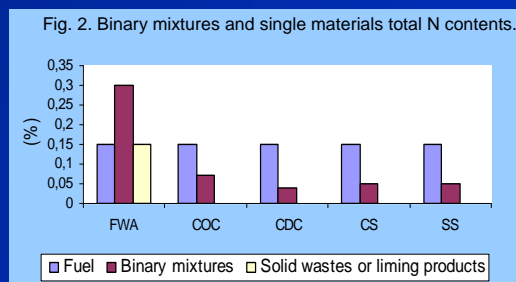
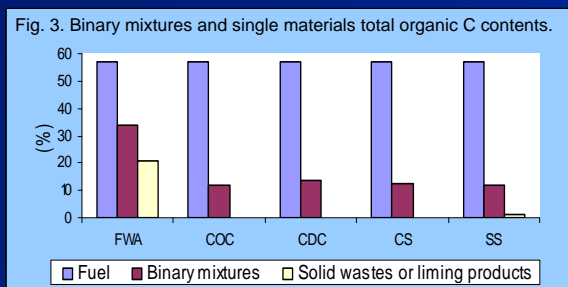


Material and methods

Fuel oil residue (F), fly wood ash (FWA), CaCO₃ rich slurry (CS), slate slurry (SS), calcium oxide (COC), charred dolomite (CDC) and binary mixtures were deeply characterized. Weight dry basis (%), pH (H₂O), pH (KCl), electrical conductivity, organic matter, total organic carbon and total nitrogen were measured by standard methods. Nutrients and heavy metals concentration was determined by ICP-OES in several extracts (distilled water, ammonium acetate 1M pH 7 and NHO₃). Hg was determined by cold vapour mercury AA in the nitric extract. A Petroflag® total hydrocarbon field test kit was tested to determine total hydrocarbons concentrations.

Results and discussion

All single materials here studied have an alkaline pH, specially COC and CDC. F and FWA presented highest organic carbon and N contents, while industrial slurries and liming products from CEDIE S.A. showed practically inexistent contents for these parameters (Fig. 1,2,3).



The previously selected physically stabilized binary mixtures showed an alkaline behaviour, considerable organic carbon and low N contents. Highest levels for C and N were obtained for F-FWA mixture (Fig. 1,2,3).

Ca, Mg, Na, K, S and P are the main available and water soluble nutrients obtained in the mixtures (Table 1).

High Ca concentrations were found in F-FWA, F-COC, F-CDC, F-CS and also very high levels of Mg in F-CDC.

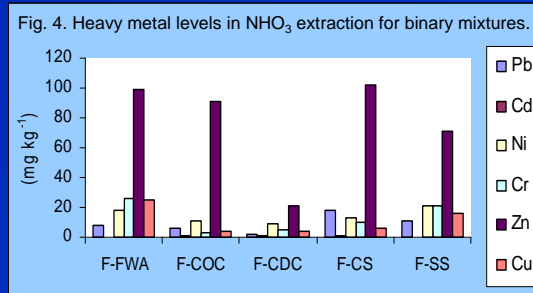
P reached acceptable concentrations only for F-FWA mixture. Obtained K values were appropriate for vegetal development in F-FWA, F-COC and F-CDC. Mixtures with slurries (F-CS and F-SS) generally presented lowest values. Referred to water soluble nutrients, high concentrations were found for Na, K and Ca in F-COC and F-CDC. K was easily mobilized in F-FWA mixture.

| Parameter (mg kg ⁻¹) | F-FWA | | F-COC | | F-CDC | | F-CS | | F-SS | |
|-------------------------------------|-------|------|-------|--------|-------|--------|-------|------|-------|------|
| | Water | Amm. | Water | Amm. | Water | Amm. | Water | Amm. | Water | Amm. |
| Ca | 55 | 5423 | 7905 | 169654 | 8795 | 107849 | 460 | 5258 | 56 | 448 |
| Mg | 41 | 589 | 0,7 | 345 | 0,7 | 4386 | 82 | 226 | 40 | 160 |
| Na | 822 | 1377 | 897 | 1040 | 714 | 1402 | 1205 | 1066 | 780 | 925 |
| K | 849 | 1952 | 365 | 440 | 252 | 440 | 53 | 67 | 52 | 83 |
| S | - | 377 | - | 326 | - | 761 | - | 914 | - | 68 |
| P | 8,6 | 41 | 0,7 | 4,2 | 0,6 | 6,8 | <0,5 | 8 | <0,5 | 4,5 |

Table 1. Some water soluble (Water) and available in ammonium acetate 1M pH 7 (Amm.) nutrient levels in binary mixtures.

No problems were detected referred to heavy metal levels in the single studied materials, neither in the selected binary mixtures, this probably due to the prevailing low concentrations and to immobilization reactions favoured by the alkaline pH's (Wong *et al.*, 2001). Metal values obtained after nitric acid digestion (Fig. 4) were remarkably lesser than legal Spanish limits for agronomic sewage sludge application (R.D. 1310/1990 BOE). In all cases except in F-CS mixture (0,324 mg kg⁻¹) obtained values for Hg were lower than detection capacity limits.

A fast field method usually employed to estimate total heavy hydrocarbons in contaminated soils was here not very successful. Too high hydrocarbon concentration (over calibration values) present in binary mixtures and in some of the waste materials studied did not let to properly use this methodology.



References

Wong J., Lai K., Su D. and Fan M. (2001) Availability of heavy metals for *Brassica chinensis* grown in an acidic loamy soil amended with a domestic industrial sewage sludge. *Water, Air and Soil Pollution*, 128: 339-353.
R.D. (1310/1990) BOE Regula la utilización de los lodos de depuración. Ministerio de Agricultura, Pesca y Alimentación.
Le Cedre. (2002) <http://www.le-cedre.fr/fr/prestige/z-produit.htm>

Acknowledgements

We are grateful to the R&D section of Plan Gallego, and to CEDIE, S.A.

Conclusions

All mixtures have an alkaline pH. The added materials contain variable amounts of nutrients such as Ca, Mg, Na, K and P, incorporating them to the mixtures, but N content remains low. No problems were detected referred to heavy metal levels. A field test method was used to assay total hydrocarbon contents without success. Binary mixtures results showed unsatisfactory nutrient values, so more studies will be made using additional products to enhance nutrient contents, getting not only suitable physical characteristics but also necessary nutrients levels to contribute to vegetation establishment in controlled acid disturb mining soils or other degraded environments.