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# Characterization of stabilized waste: Evaluation of pollution risk

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**ABSTRACT:** This study relates to the characterization of stabilized waste. Various parameters such as granulometric distribution, percentage of mineral and organic matter were estimated to appreciate environmental hazard potential and possibility of metal leaching of the samples of waste from Grange site in France. From the results, it was shown that the granulometric distribution was variable. Therefore, a strong proportion of fines (44.6 %) and medium (45.9 %) was observed due to the age of waste that supports the degradation of a great quantity of organic matter. That was confirmed by the strong mineral matter rate (63.8 %) obtained to determine the organic percentage of matter (36.2 %). The amount of heavy metals such as iron, nickel, copper, zinc, cadmium and lead was also studied. The results obtained were in a good agreement with the ones of the literature. Indeed, it appeared that iron, lead, copper, nickel and zinc are in relative strong proportion while cadmium was not very present. Iron represents 78 % of the metals. From the leaching tests, it was shown that the heavy metals concentration were very weak. Moreover, the deposit of studied waste could be a potential source of organic pollution (COD = 150 Mg C/L on average) in the case of precipitation and flood.

Key words: Ageing landfill material, organic matter, heavy metals, soil contamination, leaching test

# **INTRODUCTION**

Waste management constitutes one of the major problems for urban cities. Their production is important and in constant increasing because of the demographic explosion and the development of commercial and industrial activities. The setting in discharge of municipal solid waste represented for a long time the common way of elimination because of its low cost. However, this waste contains innumerable species that evolve progressively according complexes chemical and biological mechanisms toward stabilized waste (in last phase of degradation or not being able more to undergo degradation) (Rich et al., 2007). Indeed, it is important to note that while ageing, a landfill undergoes biologically, chemically, geologically and hydrologically mediated changes resulting in a weathering process (Bookter et al., 1982; Mata-Alvarez, 2003; Gachet, 2005; Sponza and Agdad, 2005). This low process can be divided into anaerobic and aerobic \*Corresponding Author Email: beyao@yahoo.fr

phase (Östman et al., 2006). In the literature, it was shown that stabilized waste contained an important quantity of heavy metals which were found only in very small proportion in the leachate (Christensen et al., 1996; Azita and Catherine, 2008; Ogundiran and Afolabi, 2008; Östman et al., 2008). This fact supposes that these metals either are complexed by the organic matter or trapped in the form of sulphides (Reuter and Perdue, 1977; Bruemmer et al., 1986; Ciavatta et al., 1993). This study relates to the characterization of the stabilized waste taken in a center of storage of urban and old waste from 18 to 20 y. The evolution of stabilized waste, according to the conditions of acidification, oxidation and complexation was considered in order to apprehend the future of heavy metals trapped in this waste evaluating their mobility. Indeed, it is very important to evaluate the risk for these metals to be release in water resources (Baumann et al., 2006) and grounds via an acidification and/or oxygenation of the

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tock in hidden waste (Matejka et al., 1999). The burying of the household refuse in the natural environment, apart from our spaces of life, is the oldest, less expensive and common way of the waste disposal. The increase in the production of waste, in particular within the urban community will make necessary the control of this deposit. The structures of deposit evolved in order to limit the environmental impacts. The improvement of the techniques makes it possible today to foresee new types of storage which before being dies of elimination, will be dies of valorization. Therefore, the harmful effects produced by old deposit such as olfactory effects, air pollution, soils contaminations and pollution of grounds waters remain important (Sloczynska and Slomczynski, 2004; Mwiganga and Kansiime, 2005; Shouliang et al., 2008). Few thorough analytical works on rough or pretreated waste were mentioned because of the difficulty to apply the experimental protocols and methods due to the heterogeneity of the substrate. It should be noted that in such system only the fermentable matter and paper in a lesser extend undergo the effect of degradation. Metals can evolve, but do not disappear. Great quantities of metals were thus hidden during the storage of urban and industrial waste. Table 1 indicates the concentrations of metals in waste. These contents of heavy metals were estimated according to several ways, but whatever the methods used, the results are often variable and with important uncertainties. Rouver (1990) indicates that, whatever precautions taken during the development, the execution, the analysis of the sample and the variation coefficients of measurements are generally higher than 100 due to the heterogeneity of the composition of the household refuse. The presented data related to only household refuse (or urban waste) and it should be noted that the industrial waste contains higher heavy metal concentrations (Rinke, 1999). In the sediment polluted by industrial waste, the lead (Pb) amounts vary from 1.3 to 757.8 mg/kg. Aulin and Neretninieks (1995) estimated that concentrations of Cu, Cd, Zn, Hg and Pb were 5 to 127 times higher in

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the discharges than in the original grounds. It is showed that the release of metal occurred according to two mechanisms: The saturation of the capacity plug, the changes of chemical nature which decreased the adsorption or the capacities of adsorption of toxic metals. The authors concluded that a discharge in which oxidation or oxidation-acidification occurred, the second mechanism was preponderant (Lagier, 2000; Lagier *et al.*, 2001).

## MATERIALS AND METHODS

Samples were provided from an 18 to 20 y old technical hiding and were collected at two points (2 and 3 m depth). Lixiviates came from the discharge of household refuse opened in 1974. This area, subjected to oceanic climate, is characterized by mean pluviometry (approximately 860 mm/y) and a potential evaporation of 680 mm/y. For the elution test (Wagner and Vasel, 1998) a mass of waste, crushed, dried and filtered was mixed with a defined mass of water. The ratio of both is called L/S (liquid/solid). The traditional tests of elution were carried out during 24 h with a mass of waste not exceeding 100 g of dry matter under controlled agitation. From these tests, the water soluble quantities of elements were easily estimated. Several extractions with a weak ratio L/S (for example L/S = 1) using the same elution solution provided a maximum concentration. On the other hand, a succession of elution with high ratios L/S (about 10) with solutions renewed each time gave results on the maximum extractable quantities. In the presented case, 100 g of dried, crushed and filtered waste was used. The tests were carried out with hermetic plastic bottles with a ratio of L/S = 8 under agitation during 3 to 4 days. Samples were taken at 6, 24, 48, 72, 96 h. The pH of the solutions was performed using a pH meter (TACUSSEL) and the calibration of the apparatus is carried out using 2 buffer solutions of pH7 and 4 while the conductivity was carried out using a conduct meter (LF 538 WTW). The analyses of COD was carried out according to AFNOR standards (NFT 90-101).

Table 1: Contents of heavy	metals in the household refuse
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Authors	Types of waste	Contents of mg/kg (SM)						
		Hg	Cd	Pb	Zn	Cu	Ni	Cr
Rousseau et al., 1990	Domestic refuse	3.4	5.3	268-320	634	49	16	50-70
Rousseau et al., 1990	Domestic refuse	4.8	44	556	1085	240	50	70-93
Rouyer, 1990	Urban waste	< 1	10.5	387	2259	865	200.3	426
Rinke, 1999	Urban waste	-	14.7	745	1072	235	-	-
Ranges of values	-	0.1-5	1.5-44	-	400-2300	100-900	15-200	50-100

The organic matter content is defined by the method of the weight loss (Moreno et al., 2001). Measurements of dissolved organic carbon were performed by a carbon analyzer (O. I. Analytical model 1010). After acidification of the sample by phosphoric acid, mineral carbon (CO<sub>2</sub>) was eliminated by bubbling of nitrogen. The sodium persulphate was then introduced into the sample. This oxidant reacted with the organic carbon of the sample at 100 °C to give CO<sub>2</sub>. This last was purged again and was detected by infra-red. From the CO<sub>2</sub> quantity, the carbon mass of the sample was estimated. The threshold of detection is estimated at 0.2 mg C/L. The cations and anions were performed by ionic chromatography on a Dionex apparatus DX 100. Measurements of absorbance UV were carried out using a spectrophotometer UV visible MC2 Safas with double beam of bandwidth 1nm. The precision of unit wavelength is 0.005 between 220 and 700 nm. The sequential extraction of metals from the matrix is carried out and different fractions were obtained according to the method of Tessier et al., (1979). The concentrations in metal ions such as Fe, Ni, Cu, Zn, Cd and Pb were determined by atomic absorption on a Varian Spectra AA 800 equipped with a system of Zeeman correction of non atomic absorption due to the residual matrix. The limit of detection was about 0.1µg/L and was variable according to the element proportioned. Two spectrophotometers atomic absorption flame (SAFAS) AA 181 and VARIAN AA 180 of variable limit of detection according to elements were also used. The samples were preliminary mineralized with a boiling mixture of HCl and HNO, (75% v/v of HCl) either in a Pyrex Matras or in a system of furnace microwaves according to the program of temperature XP 15000 GROUND MEL. Taking into account the interferences observed during proportioning, the analyses were carried out on masses of 0.1 g waste.

## **RESULTS AND DISCUSSION**

The granulometric distribution for the two samples is variable as shown in Table 2. Nevertheless, a high proportion of fines and means is observed due to degradation of the organic part of the waste. Table 3 illustrates chemical composition of the studied wastes. No significant difference is observed between the two samples in spite of their granulometric difference. One could expect an organic matter rate higher in the sample 2 which presents a high proportion of fines. A high quantity of iron (about 35 %) is observed. This value must be considered with carefulness because of the probable interferences (sulphates for example) during the use of absorption spectrophotometer. The evolution of the oxydable matters release as a function of the time for sample 1 is depicted by Fig. 1. It can be noted that whatever the used elution solution a stage is reached at 48 h. This stage is indication of an equilibrium state of the release potential of the waste and shows that in spite of heterogeneity in phase of waste stabilization, there is a residual release of pollution. Consequently, the deposits of waste represent potential sources of organic pollution. The follow up of dissolved organic carbon allows the estimation of the release capacity of the carbon organic matter. Fig. 2 shows the evolution of dissolved organic carbon and pH. From Figs. 2 a and c, it can be noted that the COD reaches an equilibrium states at 24 h. These states depend on the elution solution nature and translate a state of balance of the system. The stable observed value of COD seems to traduce a maximum release in the case of stabilised waste. Moreover, from Fig. 2b, an increasing evolution of the COD and pH for the bicarbonate solution is observed. The COD is the greatest part of the contaminants of subsoil waters and can influence the becoming of the other contaminants because of its implication in the complex processes such as reduction, precipitation and/or complexation. It is known not only to play a role in the transfer of heavy metals, but also to interact with the organic micro pollutants (pesticides, etc). These strong concentrations of the COD obtained by release in demineralised water and bicarbonated water would be related to the presence of strong molecular weight compounds resulting from the polymerization molecules during the process of biological degradation and even from vegetation and animal wastes oxidation (Thurman, 1985). This can support the processes of

Table 2: Granulometric distribution of waste

Granulometry	Sample 1	Sample 2	Average
% large (>10 cm)	7.40	11.6	9.40±2.96
% average (2 cm< $\Phi$ <10 cm)	52.3	39.5	45.90±9,05
% fines (<2 cm)	40.3	48.8	44.60±6.01

Table 3: Chemical composition	n of waste
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Sample	Organic matter (%)	Mineral m Other (%)	natter (%) Iron (%)	Organic C (%)	NTK (%)
N°1	36.4	33	30.6	21.5	1.5
N°2	36.0	30	34.0	17.0	0.84
Average	36.2±0.3	31.5±2.1	32.3±2.4	19.3±2.8	2.34±0.46

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Fig. 1: Sample 1 COD as a function of the contact time

complexation in hidden waste and thus influence the remobilisation of metals knowing that this organic matter can, at the same time, immobilize metals or increase their mobility (complexation by the humic substances in particular acids fulvic). However, the low values of the absorbance in the leachate shows that the organic carbon do not depend necessarily on humic substances. Consequently, the deposit of studied waste can be a potential source of organic pollution (COD = 150 Mg C/L on average) in the case of precipitation and flood. Finally, the leachate can be considered as a stabilized one. In accordance with the bibliography, the heavy metal concentrations of the leachate of Crézin are very weak as shown by Tables 4 and 5. However, a possible interference of other mineral matters is probable during the proportioning. However, this has not been studied here. The results represent average values obtained from several tests and are in the range of value of the bibliography. Pb, Cu, Ni and Zn are in strong proportion and cadmium is not present in large amount. The two analyzed samples present almost the same metals contents. The weak observed difference is due to the strong proportion of fines in the sample 2 which would result either from degradation or crushing. In this case, they would be crushed with important quantities of metals and can explain the slightly higher contents in sample 2 compared to the sample 1. These results compared with those generally obtained in old leachates come to confirm the assumption according to which an important quantity of metals remains buried in the discharges of household refuse. The sequential extraction of metals from the matrix, carried out according to the method of Tessier et al., (1979), gave



Fig. 2: COD and pH as a function of the time

five fractions. The results are depicted in Fig. 3. Copper, nickel and to a lesser extent zinc and cadmium are strongly complexed with the organic matter and sulphides. Lead is practically not complexed with the organic matter. Moreover, copper is mainly in the form of sulphide and organic complex (fraction 4). It is also found in the fraction 5, but practically non existent in exchangeable form. The affinity of copper for the

Metals

Content (µg/L)	1165	200	74	42	5	4	Metal	(mg/kg	g) (1	ng/kg)
Precision (µg/L)	$\pm 6$	$\pm 6$	$\pm 5$	$\pm 2$	$\pm 2$	$\pm 4$	Cd	± 2		15.6
Content (µmol/L)	21	3.4	1	0.6	-	-	Cu	± 3		225.8
							Ni	± 3		131.7
							Pb	± 5		339.4
							Zn	± 2.5		198.9
8	100 - 80 - 60 - 40 - 20 -									
		Cu		C	u		NI	PO	ZII	
						неаvy	metals			
						Sam	ple 1			
			🗖 frac	tion 1 🗖	fraction	2 🗖 frac	tion 3 🗖 fractio	n 4 🗖 fraction :	5	
	100									

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Pb

Table 4: Contents of metals in the lixiviate of Crézin Ni

Cu

Zn

Cd

Fe



Ni Heavy metals Рb

organic matter is often evoked in the literature (Mårtensson et al., 1999; Rinke, 1999; Lagier, 2000; Berthe, 2006). Copper appears the weak and strong organic complexes molar mass which can be formed in

Cd

Cu

80

60

40

20

0

%

the phase of acidogenesis and methanogenesis. The strong proportion of copper in fraction 4 is explained by its fast adsorption on the surface sites compared to other metals. Moreover, nickel is distributed uniformly

Zn

Table 5: Contents of heavy metals in stabilized waste

Sample 1

Sample 2

(mg/kg)

16.6

362 144.8374.7 219.6

Precision

in fractions 2 and 3. Lead presence in fraction 3 and 4 accounts for approximately 98 % of the total content while in the residual and organic fraction it is in very small proportion. Cadmium and zinc present intermediate speciation with prevalence for fraction 3. These connections with oxyhydroxides of iron and manganese are well known in the literature (Rinke, 1999). All studied metals (Cd, Cu, Ni, Pb and Zn) are in small proportion in fraction 1. However, some of them such as Cd and Zn are found in strong proportion in fraction 3. This fact can be explained by the increasing of the pH and redox potential  $E_{H}$  during the stabilization phase of waste. Another explanation related to the operating conditions of the sequential extraction can be considered. Indeed, it is possible that during the extraction, part of exchangeable metals could be adsorbed on the oxide-hydroxide ferric phase formed under aerobic conditions. The results obtained with sample 2 confirm the distribution observed with sample 1. However, the proportions observed for the refractory fraction are weak compared to those of sample 1 except for the copper which presents the same contents in fractions 4 and 5.

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