# Study of two sampling procedures for the valorization of metal hydroxide sludge as pollutant trapper

Valérie Laforest, Loïc Perrin, Jacques Bourgois

# Study of two sampling procedures for the valorization of metal hydroxide sludge as pollutant trapper

**Valérie Laforest**
**Ecole des Mines de Saint Etienne, centre SITE**
158 Cours Fauriel 42023 Saint Etienne, France,
E-mail : laforest@emse.fr

**Loïc Perrin**
**Ecole des Mines de Saint Etienne, centre SITE**
158 Cours Fauriel 42023 Saint Etienne, France,
E-mail : perrin@emse.fr

**Jacques Bourgois**
**Ecole des Mines de Saint Etienne, centre SITE**
158 Cours Fauriel 42023 Saint Etienne, France,
E-mail : bourgois@emse.fr



**Abstract:** For the valorisation of metal hydroxide sludge as adsorbent of pollutant, it is necessary to make sure that the adsorption matrix (sludge) has characteristics allowing a reproducibility of the valorisation operation. Taking into account the heterogeneity of this solid waste in terms of nature and metal chemical composition, it is necessary to establish if this heterogeneity will have important consequences on the adsorption yield of these sludge. Thus, the study, is relative to the influence of the composition of metal hydroxide sludge on their adsorption properties. Two sampling procedures are studied: sampling in a continuous way at the drying step or by coring of the final sludge heap. In order to compare the properties of adsorption, each sample is tested according to a definite adsorption protocol. In addition, this study makes it possible to compare the two sampling procedures and to determine their relevance to the sample technique. The first results show that the methods make it possible to obtain close results, both for adsorption and sludge composition. Moreover, successive quartering permits to have a representative sample in terms of metal composition.

**Keywords:** valorisation, sampling, polymetallic hydroxide sludge, metal finishing treatment, $Cr^{VI}$

## 1 Introduction

Industrial aqueous pollution (heavy metals) accounts for 30 to 40% of all industrial pollution. Metal finishing is one of the sectors which contribute mostly to this pollution. Due to its unique production, metal finishing consumes and discharges wastewater containing metallic ions, cyanide, COD, etc.. Therefore, this activity has been bound to the European Integrated Pollution Prevention and Control Directive since 1996, known as the “IPPC Directive” [1]. In France, this directive is applied “as is” for metal finishing workshops through the ministerial

order of the 30th of June 2006. Before 1996, this text was already belonging to the legislation of the officially identified sites under the 2565 codification for the protection of the environment [2]. This ministerial order defines thresholds in terms of pollutants in the effluent and in terms of flow rate and concentration of specific chemical species for this branch of activity. These workshops must implement curative or preventive Best Available Techniques (BAT) which are another major principle of the IPPC Directive [3]. For about 65% of all workshops, initiatives and actions designed to limit environmental impacts are typically curative. Concerning wastewater composed mainly of heavy metals, the detoxication process of wastewater is the precipitation of metal ions in hydroxide. Some species such as chromates may require an oxidation/reduction treatment. After filtration, hydroxides obtained as sludge are disposed of in various sectors. This sequence of processes is described in the BAT reference documents (BREF), on "Best Available Techniques for metal finishing treatment and plastic finishing treatment" [4]. It is important to note that France produces 180 000 tons of metal sludge per year compared to the data in Europe (950 000 tons per year) (source CETIM). Currently, despite of the existence of processes such as hydrometallurgy for sludge rich in zinc, pyrometallurgy for sludge rich in nickel, thermal reconditioning for sludge with specific characteristics or finally added to cement for sludge riches in aluminium or iron, polymetallic hydroxide sludge (predominance of non-metal) are mostly eliminated in hazardous waste landfills. For these reasons, the objective of this research project is to propose a new method for the valorisation of polymetallic hydroxide sludge that can not be valorised by the methods of treatment mentioned previously because of their characteristics.

Another key problem of the metal finishing industry deals with chromium. Indeed, its' use in metal finishing applications is quite widespread. It gives at a piece different properties such as hardness, aesthetics, and resistance to temperature, corrosion or wear. This versatility justifies that the chromium is an essential element for various applications. The most widespread properties of the chromium metal deposit are their protective and decorative characteristics. It is estimated that 30 000 to 32 000 tons of chromic acid per year are used in metal finishing at the European level. Because of drag-out all along the production line, 20 to 60% are found in industrial aqueous effluents. This ratio depends on the local context of each workshop, namely its size and recycling measures implemented. So, it appears that the decontamination of chromium is very important for the metal finishing industry.

This article concerns a part of the project previously presented. In fact, for the valorization of metal hydroxide sludge as pollutant trapper, it is necessary to make sure that the sorption matrix (sludge) has characteristics allowing a reproducibility of the valorization operation. Taking into account the heterogeneity of this solid waste in term of nature and metal chemical composition, it is necessary to establish if this heterogeneity will have important consequences on the sorption yield of this sludge. The study, thus, relates to the influence of the composition of metal hydroxide sludge on their sorption properties. Two sampling procedures are studied: sampling in a continuous way at the drying step or by coring of the final sludge heap. The $Cr^{VI}$ is taken as the pollutant for this study.

## 2 Objectives of the study

The purpose of this study is relevant to the poly-metallic hydroxide sludge (pMHS). The objective is to determine what sampling method is most appropriate in order to obtain a chemical composition for sludge as homogeneous as possible. The change in the chemical composition of pMHS could affect the sorption capacity of pollutants. The establishment of a sampling would ensure reproducibility of sorption experiments. It needs to be fast and easy to

implement. The experiments of sampling are realized. Its' utility and representativeness depend on the obtained results of composition and adsorption. The main purpose of the waste sampling is similar to the pMHS sampling for the characterization and the determination of their properties. An important feature, which applies to most deposits of waste, is the great diversity of sources, both in time and in space. This will lead to difficulties when it comes to a constant sample. For this reason, different sampling methods were introduced.
The Research Center BRGM [5] presents a summary of recommended methods for the final sample according to the state of waste (liquid samples, concentrated paste samples, solid samples). The three main sampling methods [6] are as follows:

- The *simple random sampling* where the population has the same theoretical chance of being selected in the sample: This sample is perfect if all variations in the population are represented.
- The *stratified random sampling* is more complex, and is used for heterogeneous populations. The criterion of stratification must have a close relationship with the studied variable. In other words, people are stratified so that within each party or stratum, fluctuations of the variable (i.e for household waste, standard of living, waste production, household size, ...) are minimal. After this stratification, random sampling (single or systematic) is done in each stratum. The number of samples of each stratum can be determined either by proportionality to the public, either through optimization, ie that the sample is selected so that the variation of the average is the lowest possible for the sample size.
- The *systematic random sampling* is sometimes the only solution that can be implemented. Each element of the population is randomly selected. But the drawback of this technique is on the low accuracy of results when the population covered by the sampling, a trend or unknown non-systematic variations.

Concerning pMHS, the sampling method to be used is certainly closer to the stratified random sampling. Indeed, the sludge composition is not constant ("heterogeneous population"). In addition, the sampling method is most representative. Depending on waste nature, different sampling techniques are created:

- **Clinkers** of Incineration plant of household waste [7]
- **MODECOM Method** for household waste [7,8]
- **Ground** [9,10]
- **Sludge:** Quartering successive method: the aim is to divide the sample into four parts. Two opposing quarters are excluded, and the two remaining combined. Then this process is repeated until a properly sized sample is obtained. [11,12]

In France, the ministerial order of 8$^{th}$ January, 1998**,** appendix V **«**sampling method for a batch of raw sludge [...] and composted» describes the experimental protocol. It consists in ensuring a representative sample, i.e. twenty-five points evenly distributed in different depths and different batch of the sludge to be sampled. The capacity of samples taken is not specified. The samples must be taken outside of the crust and surface areas of water accumulation. The various samples are mixed, homogenized and reduced to a global sample of one kilogram approximately. [13]

Finally, in our case study, the sludge collection is done randomly and quartering is used as the sample reduction method.

# 3 Experimental protocols

## 3.1 Method

After the sludge samples have been taken, they are homogenized and reduced by quartering modeling. Then, sludge is grinded and suspended in a solution containing the pollutant to trap. After that, the mixture is filtrated and the liquid phase is analyzed by ICP. The general protocol used is presented in the figure 1 [14].

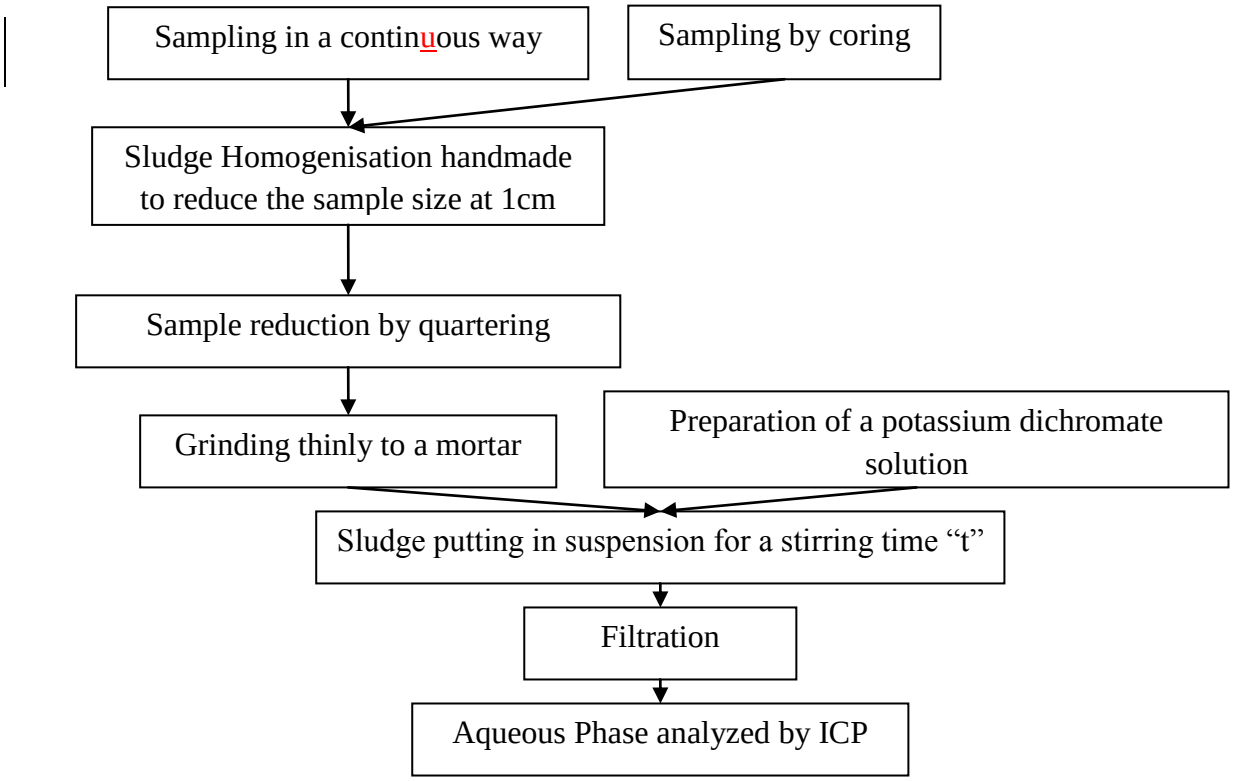



**Figure 1 : general protocol**

## 3.2 Sample reduction method

The sludge sampling is done directly in the industrial workshop. The sludge reduction is done in the laboratory room using the quartering method. The raw sludge is disposed in a circle which is divided in 4 parts. Two opposite parts are thrown out and the two others are mixed together. This operation is repeated until 50g of sludge are obtained. The initial sludge is noted "sample 0", the sample of the first reduction is named "sample 1" and so on until "sample n". The figure 2 presents the step.

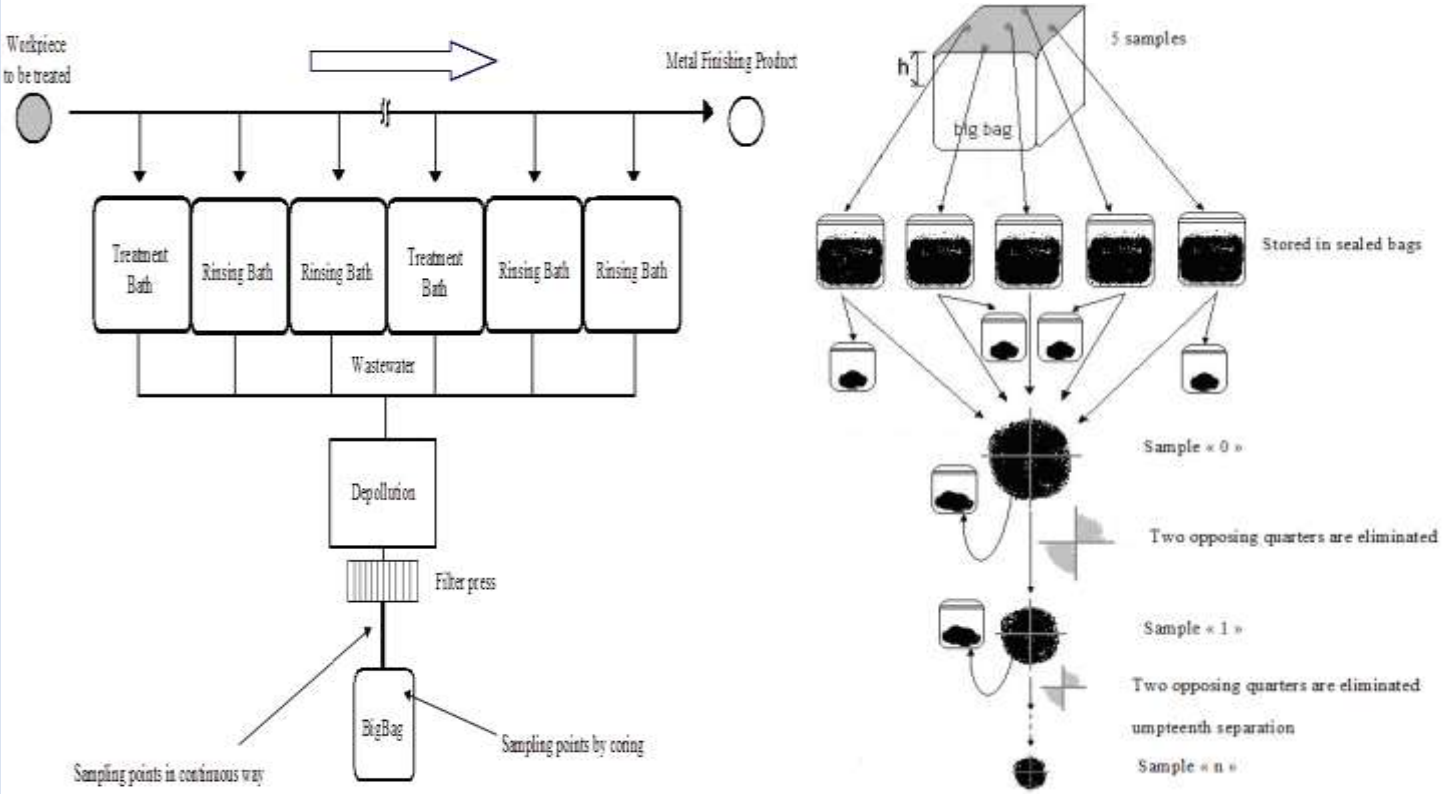



**Figure 2 : sampling points and sample reduction method**

*Nota: the notation of each sample is composed by one letter and two numbers. For example the sample written C31 is a sample taking in continuous way for the big bag 3 corresponding at the first reduction and the sample written T26 is a sample taking with the trepan in the big bag 2 corresponding at the sixth reduction.*

### 3.3 Sorption protocol

A mass "m" of $Cr^{VI}$ is weighted. A stock solution is then prepared with distilled water in a flask of 500 mL. In order to homogenize, the solution is stirred several times. Then, 25mL are taken and blended with 50 mg of sludge. The solution is stirred during a time "t" and filtrated. The liquid part is analyzed with ICP. Figure 3 presents the stirring and filtration steps.

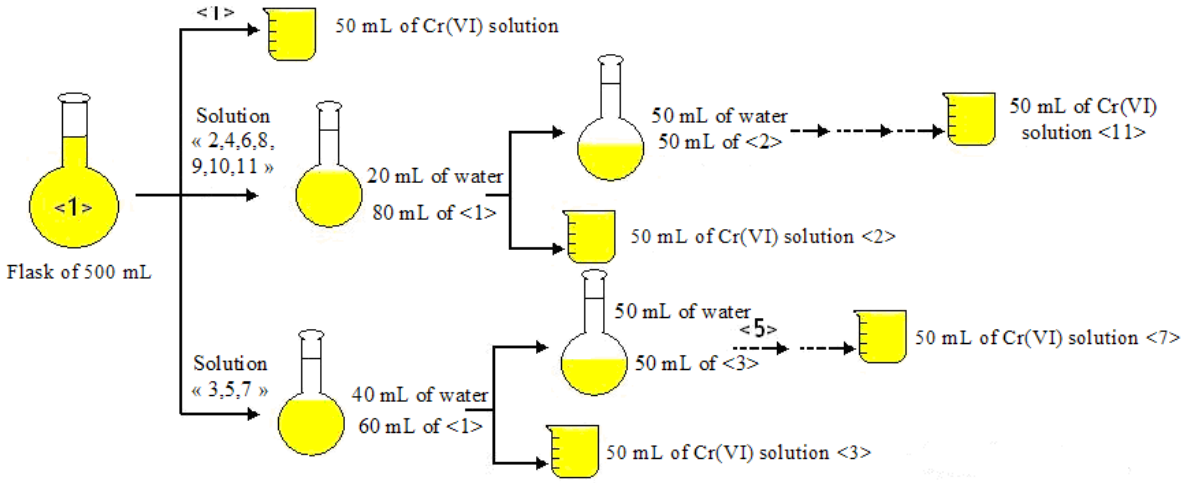



**Figure 3 : sorption protocol**

### 3.4 Sludge dissolution protocol

250mL of hydrochloric acid (35%) is diluted in fresh distilled water in a 500mL flask. 40mL of this solution is sampled and blended with 50mg of sludge. The solution is stirred during 30 min. After filtration, the clarifying solution is analyzed with ICP.

## 4 Experimental results

### 4.1 Sorption duration

Because of the industrial application targeted by the project, it is necessary to have a laboratory experimental protocol applicable to industrial scale and running. Thus, in order to determine which duration of sorption is optimal, a first range of duration has been tested. Two durations of sorption experiments have been done and are presented here: 2 hours and 13 hours.

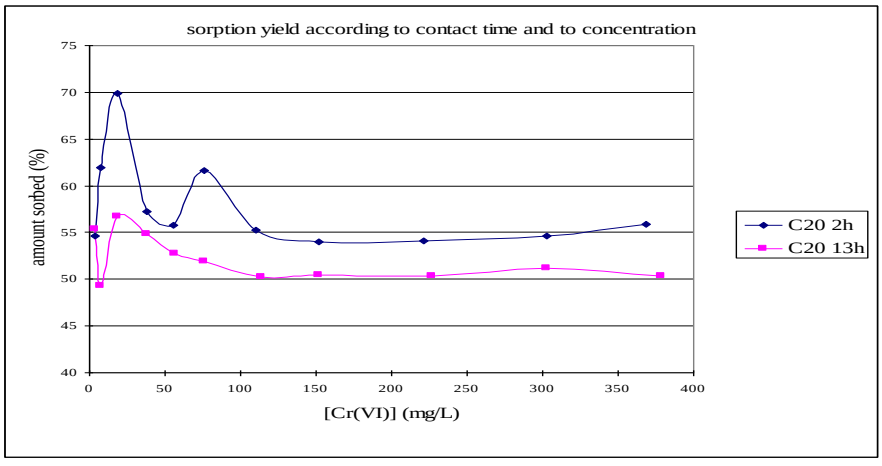



**Figure 4 : sorption yield according to sorption duration**

One can observe on figure 4 that:

- Sorption rate seems to be stable for concentration of $Cr^{VI}$ in the media greater than 100mg/L

- The difference of sorption yield seems to be insignificant for an industrial application: 50% for 13 hours of sorption and 55% for 2 hours of sorption (moreover, experimental error is estimated at 4%)

Then we have decided to experiment with sorption duration of 2 hours.

### 4.2 Sorption yield

In order to assess if the two sampling methods tested permit to obtain homogeneous sludge, sorption experiments of $Cr^{VI}$ have been conducted. The results presented in this article concern two different big-bags: no. 2 and no. 3. Sorption yields according to [$Cr^{VI}$] are presented.

Figure 5 presents the results for continuous sampling and the results for the coring method of sampling and both for big-bag 2

Figure 6 presents the results for continuous sampling and the results for the coring method of sampling and both for big-bag 3.

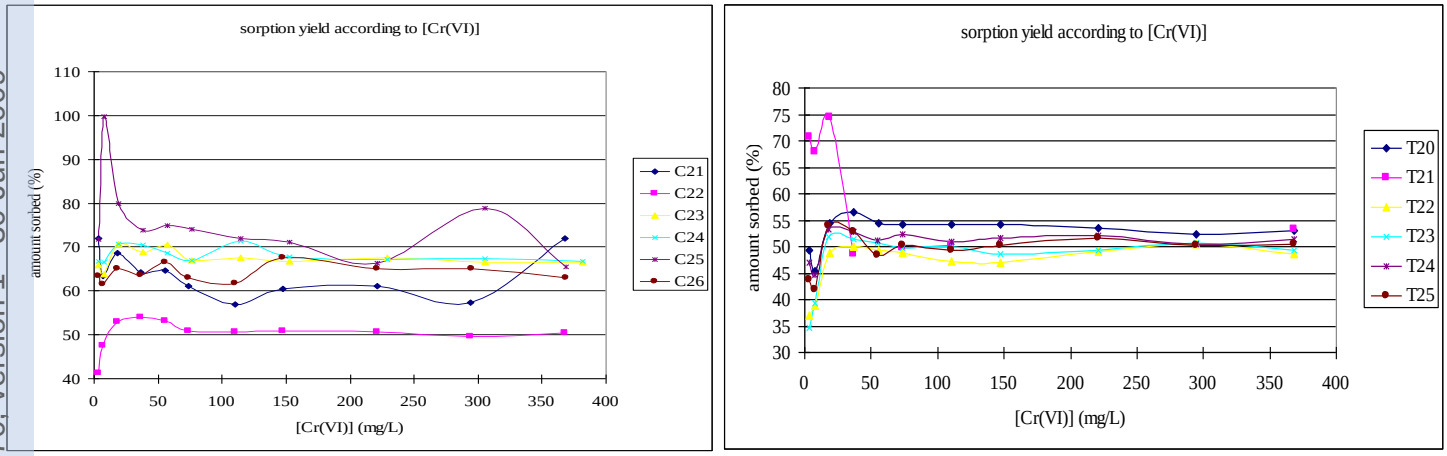



**Figure 5 : sorption yield according to [$Cr^{VI}$] for the big bag 2**

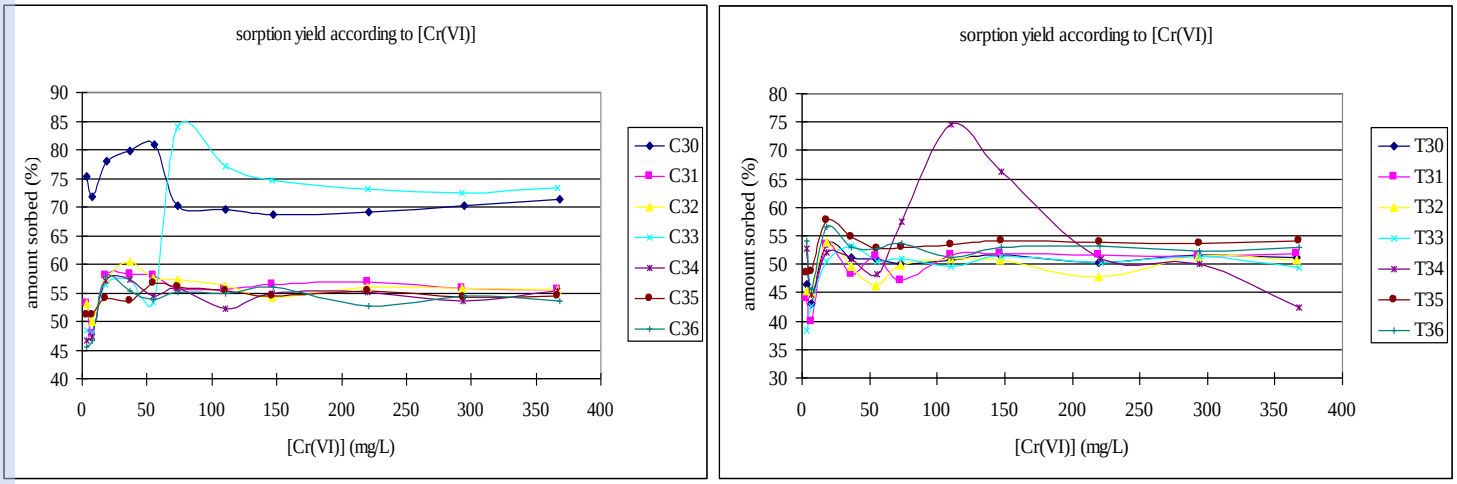



**Figure 6 : sorption yield according to [$Cr^{VI}$] for the big bag 3**

Irrespective of the big-bag, one can conclude that the reproducibility of the sorption of $Cr^{VI}$ is higher for the coring method of sampling.

Moreover, the reduction steps do not seem useful because results are quite the same for a concentration greater than 100mg/L in $Cr^{VI}$.

### 4.3 Composition of the big bags

Sorption yield depends on the composition of the sludge and the performance of the precipitation. In order to determine the composition of the sludge, to check the homogeneity of the sample and to determine if a sampling method is more pertinent, analysis of samples have been conducted. Two dissolutions of each sludge sample have been carried out: one in the water and one in hydrochloric acid.

#### 4.3.1 Dissolution in water

The result of sludge dissolution in water is demonstrated in figure 7.

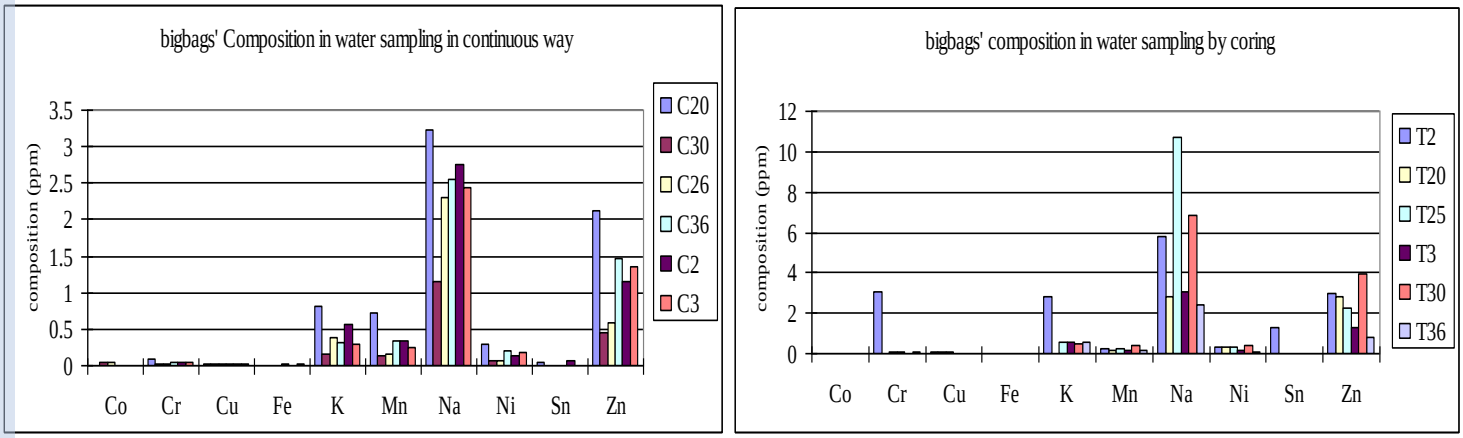
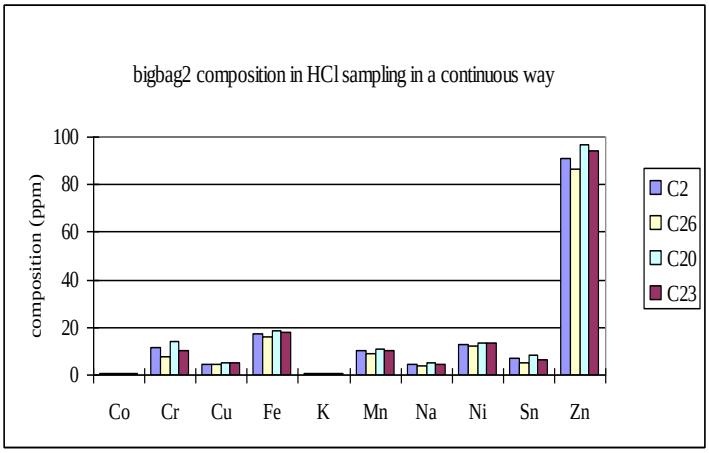



**Figure 7 : big bags' composition in water**

Irrespective of the sampling method (continuous way or coring way), one can observe that the chemical species in the solution are the same and samples are more concentrated for the coring way.
We can observe that K, Mn, Na, Ni and Zn are present in the sludge.

#### 4.3.2 Dissolution in acid solution

The result of sludge dissolution in HCl is demonstrated in figure 8.



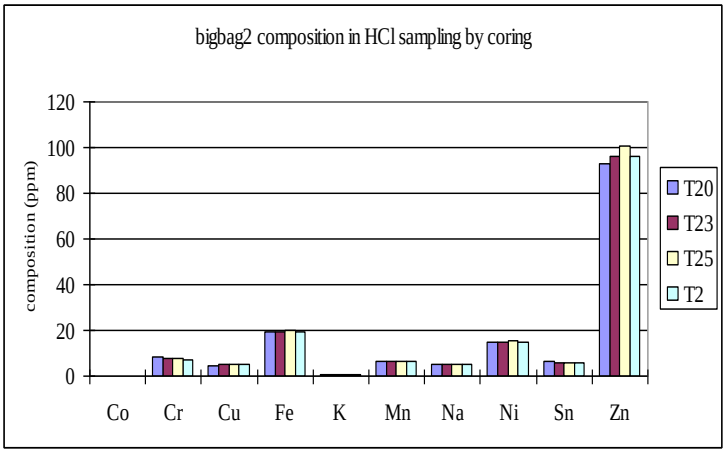
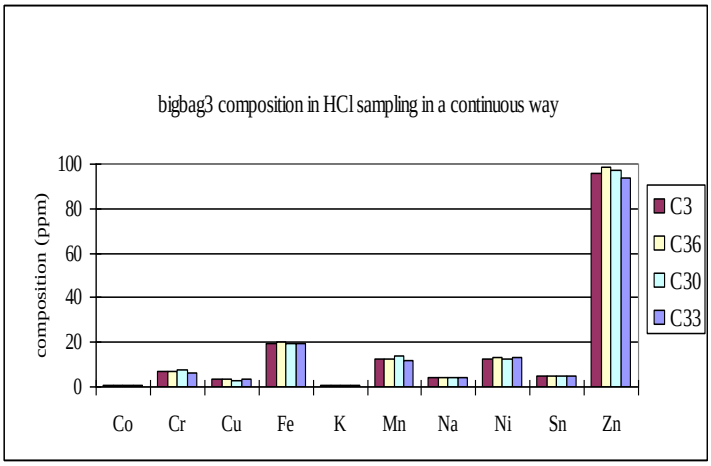




**Figure 8 : bigbag2 composition in HCl**



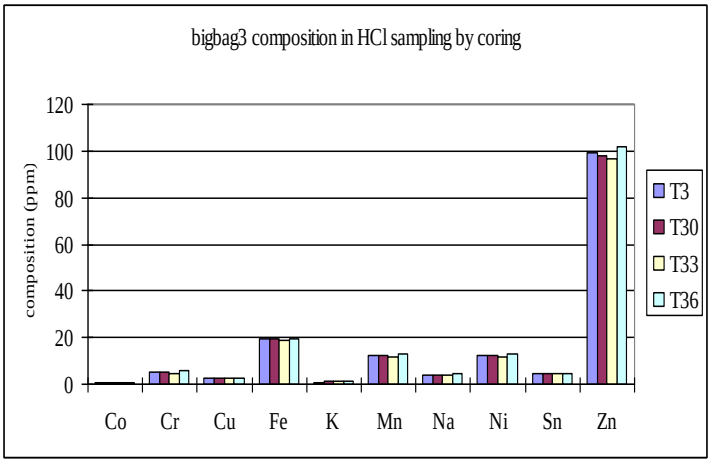




**Figure 9 : bigbag3 composition in HCl**

Irrespective of the sampling method (continuous way or coring way), one may observe that the chemical species in the solution are the same and their concentrations are quite equal.
We can observe that Cr, Cu, Fe, Mn, Na, Ni, Sn and Zn are present in the sludge.
The difference of species in the acid solution and aqueous solution is due to the solubility of metal hydroxide for low pH.

## 5 Conclusion

The objective of the study presented in this article is the validation of a sampling procedure for the valorization of metal hydroxide sludge as pollutant trapper. The experiments conducted permit to draw the following conclusions:

- Sorption results highlight a better reproducibility of $Cr^{VI}$ sorption for the samples taken with an trepan,
- Sample composition is the same and do not allow by themselves to validate the choice of a sampling procedure,
- Reduction steps seem to be useless because we have observed that sorption yields are the same whatever the reduction for a concentration in $Cr^{VI}$ greater than 100mg/L

Then, if we want to check if the hydroxide sludge have the capacity to trap $Cr^{VI}$, optimal sampling conditions are:

- A sampling with a trepan
- No sampling reduction i.e. adsorption on the raw sample

Moreover, it is of interest, on the one hand, a gain on personnel costs for the sampling on an industrial site and, on the other hand, a time gain in preparation before sorption.

**References**

[1] Directive IPPC directive du conseil 96/61/CE du 24 september 1996 (modifiée en 2008) concernant la prévention et la réduction intégrées de la pollution, J.O.C.E. n°L 257 du 10 octobre 1996. 24 article, 5 annexes. http://europa.eu.int/comm/environment.ippc/, 2008.

[2] Arrêté du 30 juin 2006 relatif aux installations de traitement de surfaces soumises à autorisation au titre de la rubrique 2565 de la nomenclature des installations classées. 2006.

[3] A.Cikankowitz, Méthodologie d'évaluation des performances environnementales de procédés en vue de les comparer et les valider aux meilleures techniques disponibles, PhD Thesis Sci, 2008.

[4] BREF**,** Bureau européen pour l'IPPC. *IPPC BREF* outline and guide. http://eippcb.jrc.es/pages/FActivities.htm, 2008.

[6] BRGM
www.sites-pollues.ecologie.gouv.fr/.../guidesevaluations/evaluationsimplifiee/telechargementesr/an06.pdf, mars 2000

[6] S.Ould Aloueimine, Méthodologie de caractérisation des déchets ménagers à Nouakchott (Mauritanie) – Contribution à la gestion des déchets et outil d'aide à la décision. Université de Limoges, avril 2006.

[7] V.Nouvel. Cours de déchets « Echantillonnage et Caractérisation d'un gisement de déchets ». Rennes , 2005.

[8] B.Morvan en partenariat avec le Cemagref de Rennes, Caractérisation de déchets. Rennes, 2005.

[9] M.Girard, C.Walter, JC.Rémy, J.Berthelin, JL.Morel. Sols et Environnement. Paris, Dunod, 2005.

[10] P.Delage, B.Schreffer. Géomécanique environnementale Sols pollués. Paris, Lavoisier , 2005.

[11] Centre d'expertise en analyse environnementale du Québec. Programme d'accréditation d'échantillonnage environnemental. Protocole d'échantillonnage des matières résiduelles fertilisantes (Résidus de fabriques de pâtes et papiers et autres résidus solides. Québec, 2006.

[12] Arrêté du 8 janvier 1998 fixant les prescriptions techniques applicables aux épandages de boues sur les sols agricoles pris en application du décret n° 97-1133 du 8 décembre 1997 relatif à l'épandage des boues issues du traitement des eaux usées

[13] Trame, Agriculteurs Composteurs de France. Charte de bonnes pratiques de compostage agricole, fiche méthode n°5, méthode d'échantillonnage, 2004

[14] C.Lannes, Rapport de projet industriel : Identification et expérimentation d'un protocole d'échantillonnage des Boues d'hydroxydes poly-métalliques, Ecole Nationale Supérieure des mines de Saint-Etienne, 2008