

BENEFIT AND LIMIT OF FROTH FLOTATION TECHNIQUE TO REMOVE HEAVY METALS FROM SILT FRACTION OF CONTAMINATED SEDIMENTS

A WALLONIA (BELGIUM) CASE STUDY

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ABSTRACT

A case study at laboratory scale on Wallonian (Belgium) dredged sludge is presented, pointing out the benefits and limits of froth flotation technique on silt fraction of fresh sediment. This fraction is coming from a more general treatment of sediment (mainly wet size separation by sieve, screw classifier and hydrocyclone) to obtain five fractions: gravel, coarse sand, fine sand, silt and clay. In sediment from Wallonia, particles with grain size below 70 μm can represent more than 60 wt. % and trap most of the micropollutants (heavy metals and organic compounds) so the need to treat them. Effects of different reactants (anionic collectors) are presented in combination with various frothers to improve the selectivity of the treatment. Emphasis is put especially on Pb and Zn removal, as they are frequently the heavy metals encountered in Walloon dredged sludge. The benefit of flotation is demonstrated here, but emphasis is put on the need to adapt the protocol to each sediment fraction characteristics.

Keywords: Froth Flotation, Silt Fraction, Heavy Metals, Dredge Sludge

INTRODUCTION

The management of dredged sediment is an issue in Wallonia, as in other parts of the world. Indeed, natural sedimentation in canals and waterways over time tends to limit their ability for water transport, when at the same time there is a European will to promote a more sustainable way for the transport of goods.

Moreover, the management of natural resources, including mineral ones, in a more sustainable way is emerging as a priority for governments and companies linked to environmental considerations, due to the worldwide market of raw material. Therefore, dredged sediments could represent a useful mineral raw material for various local industries depending on their intrinsic characteristics and should be considered as potential secondary raw material, useful to maintain industrial activities on the territory in a circular economy approach.

At the present time, dredging operations have an important cost and the removed sediments have only few to no use. Even worse, they are considered as waste (dangerous or not, depending on their pollutant contents) which are mainly disposed in landfill at high cost (multiplied roughly by a factor 10 to 20 over the last 20 years in Wallonia).

It is estimated by authorities in charge and dredging sector that a minimum of 300.000m³/y should be removed in order to insure the minimal required transport capacity, since 365 km over the

450 km existing waterways of Walloon canals are at European Gauge '1350t' or more, and there is a political will to upgrade 330 km at Gauge Va or more (2000t or more) for 2025. In addition, there is still a background of (at least) 2 Mm³ of historical deposit due to full stop of dredging activities between 1996 and 2001.

There is also a consensus on the amount of polluted sediment present (typically 65 to 70% of dredged sediment) containing heavy metals and organic compounds in such amount that prevents direct elimination (i.e. without adapted treatment) or use as secondary raw material according to the actual legislation. Wallonia legislation [1] defines two types of sediment depending on their pollution content (based on the analysis of 9 metallic elements and chemical families such as Borneff's HAP, Ballschmieter's PCB and hydrocarbon). For each element or chemical family, the legal text gives two thresholds respectively for class A and class B sediments. If none of the pollutants sought is detected at a level higher than threshold of class A, then the sediment is declared not polluted. When there is a pollutant analysis over threshold of class B for at least one of the elements or chemical families, it is declared polluted. Complementary tests based on leaching assays are performed in the intermediate case, in order to determine the final status of the sediments. Class B (polluted) sediments need a treatment before disposal, even as waste. Such treatment is typically a step of purification or

stabilization. In that case, mineralurgical approach is often proposed as a possible way to reach regulatory levels at a reasonable cost. In particular, the step of purification itself could be performed by froth flotation, using the experience of mining and extracting industry.

CTP developed a flow sheet of sediment's treatment mainly based on a particle size separation (sieve & screen, screw classifier and hydrocyclone) [2] to obtain five fractions: gravels, coarse sand, fine sand, silt and clay. This treatment leads to the concentration of most of the pollutants in the finest fractions of the sludge i.e. in silt (-70 +10 μm) and clay (-10 μm). Consequently, these fractions should be purified before being valorised. The purpose of this study is to investigate the possibility to apply flotation technique to the contaminated silt fraction coming from SOLINDUS treatment in order to remove heavy metals in a real case study. The present work focuses especially on Pb and Zn, which are pollutants that are the most frequently encountered in Wallonia dredged sludge.

MATERIALS AND METHOD

Dredged Sludge Sampling

During the course of SOLINDUS project, the strong collaboration with the authorities led to the possibility to take part in the dredging operations, at least for sampling purpose. Indeed, it was possible, with the help of the dredging companies in charge, to collect roughly 10 to 50m³ of wet sediment on various locations throughout the region. Over the last five years, twelve sampling operations were conducted for the benefit of the systematic characterization and treatment. Four representative Wallonian dredged sludge coming from Obourg (S1), Nimy-Blaton (S2), Dampremy (S3) and Seneffe (S4) were selected in order to establish the methodology needed to find the best flotation protocol to apply, based on previous experience and speciation tests of the metallic trace elements (results not presented here) following Tessier Method [3].

Mineralurgical Treatment

The flow sheet developed for a treatment of dredged sludge by mineralurgical techniques is a batch process based on wet particle size separation, with four main steps (Figure 1). Once homogenized, the dredged sludge is screened to remove the solid matter with a size exceeding 2 mm (pieces of tires, wood, gravels...). Coarse sand fraction (-2 mm +250 μm) is obtained after treatment on sieve bend. The third step of granulometric separation is performed by a combination of screw classifier and hydrocyclone, which leads to the separation of the fine sand (underflow) from even finest particles (overflow). A last step of hydrocycloning make the separation

between the silt fraction (-70 +10 μm) and the clay (-10 μm). When the silt fraction remains polluted after such a process, flotation technique is applied. Since the full process was set up at pilot scale, including two flotation cells of 750 litres each, preliminary trials were performed to identify the appropriate reagents and operating conditions. This paper will exhibit results obtained at laboratory scale (to limit the amount of matter used), but with the aim at upscaling it at a later stage. Only the silt fraction obtained after SOLINDUS treatment will be considered here as a starting material for the laboratory flotation study.

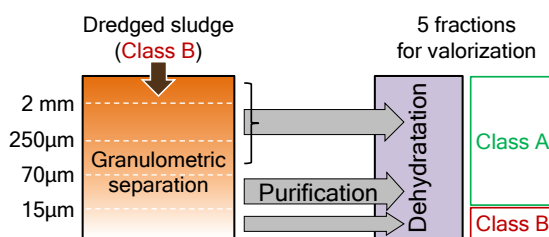


Fig. 1 Solindus process'scheme used to prepare silt fraction from sampled dredged sludge.

Flotation Cell Experiment

Flotation is a solid-solid separation technique based on differences in wettability between the particles. The principle is to introduce air bubbles in a suspension, where different reagents help to separate rather hydrophobic from rather hydrophilic particles. The hydrophobic particles are preferentially fixed on the surface of bubbles which are recovered by the means of a stable froth layer produced by the addition of frothing agents. When the hydrophobic character of the particles is not sufficient to ensure a selective separation, a conditioning step of the slurry is necessary by adding flotation reagents like non-ionic, cationic or anionic collectors [4]. The use of froth flotation as a remediation technique for material polluted by heavy metal, like sediment and soil, was largely investigated [5-11].

Flotation experiments were carried out in a laboratory mechanical cell (Denver D-12, volume 5 l) using the silt fraction (-70 +10 μm) as obtained from SOLINDUS separation treatment at 20 wt. % of solid content and diluted with tap water as necessary to reach a pulp density between 10 and 15%, considered as an optimum from previous studies [12]. The froth (concentrate) was collected separately after each flotation step, when the tailing is the residual material recovered.

Anionic collectors were chosen, based on previous studies on other sediments and with the help of metal traces speciation tests showing that Zn is rather linked with iron oxide species, Cu linked to organic matter, when Pb, Cr and Ni were linked to the residual and most stable compounds, giving a first

estimation from the easiest to the hardest element to remove by flotation.

Different experimental protocols were investigated using either alkyl succinamate (Suc) alone or in combination with petroleum sulfonate (Sul), or either potassium amylxanthate (KAX) alone or in combination with ethylxanthate (KEX) as collectors. Polypropylene glycol monomethyl ether (PGME) or methyl isobutyl carbinol (MIBC) were also added as frothers. Such protocols were first tested on silt fractions S1 and S2 and adapted to Silt fractions S3 and S4.

For the protocol using Suc or/and Sul (called P1 series), trials are including a conditioning step of 20 min where a dispersant (Na_2SiO_3) is added, together with the collector(s) and under continuous agitation at 1140 rpm, followed by 4-6 min flotation step. Up to two or three successive sequences were performed after the initial one, with a conditioning time of 8-10 min and a flotation time of 4-6 min. Concentration of reagents used at each step are summarized in Table 1 to 4.

For the protocol using KAX alone or in combination with KEX (called P2 series), a conditioning step of 12 min was set where Na_2SiO_3 is added, together with the collector(s) followed by 4-6 min flotation step. Two other successive sequences were performed after the initial one, with conditioning a step of 2-3 min and a flotation time of 4-6 min. Continuous agitation speed was maintained at 1140 rpm during all the process. Concentration of reagents used at each step are summarized in Table 5 and 6.

Determining the optimum flotation conditions means at least to obtain stable froth, and then two parameters should be taken into account: The first is the quantity of mass floated, and the second is the heavy metals concentration in the flotation concentrates, compared to the initial concentration in the feed. Ideally, a selective method should allow the removal of an important part of a specific pollutant in the lowest quantity of concentrate.

The results presented in this paper will focus especially on the comparison between initial Pb and Zn content and remaining amount of those elements in the tailings. They are the main pollutants found in the sediments sampled, and are often encountered in different places of dredging in Wallonia. Of course the final evaluation of the efficiency of the treatment is depending of the environmental regulation (under revision since 2014).

In protocol P2, sulfurization of minerals oxides was performed by adding sodium sulfur (Na_2S , $3\text{H}_2\text{O}$) with the aim at better collecting Zn associated with the oxide fraction (as established from speciation tests). The exchange between MIBC and PGME from one protocol to the other was only based on previous experiment and the visual aspect of the froth, with the goal to keep it stable and with a significant thickness.

Table 1 Concentration (g/t) of reagents used for protocol based on Sul/Suc (P1) on S1.

Sequence	A	B	C
Na_2SiO_3	750		
Suc	100	100	100
MIBC	160	100	100

Table 2 Adapted conditions and concentration (g/t) of reagents for trials on S1 and S2 (P1*).

Sequence	A	B	C	D
Na_2SiO_3	750			
Suc	100	70	50	50
Sul	100	50	50	50
PGME	60	40	20	

Table 3 Adapted conditions and concentration (g/t) of reagents for trials on S3 (P1**).

Sequence	A	B	C	D
Na_2SiO_3	820			
Suc	350	260	170	90
Sul	310	240	160	80
MIBC	160			

Table 4 Adapted conditions and concentration (g/t) of reagents for trials on S4 (P1***).

Sequence	A	B	C
Na_2SiO_3	500		
Suc	200	150	100
Sul	200	150	100
MIBC	100		

Table 5 Concentration (g/t) of reagents used for protocol based on KAX/KEX (P2) on S1 and S2.

Sequence	A	B	C
Na_2SiO_3	500		
$\text{Na}_2\text{S}, 3\text{H}_2\text{O}$		1000	1000
KAX	100	50	50
PGME	50	50	50

Table 6 Adapted conditions and concentration (g/t) of reagents for trials on S3 and S4 (P2*).

Sequence	A	B	C	D
Na_2SiO_3	750			
$\text{Na}_2\text{S}, 3\text{H}_2\text{O}$		4500	4500	3000
KAX	300	450	300	
KEX				450
MIBC	150			

Elemental Metallic Trace Analysis

The total concentration of metals trace elements considered as pollutants (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) was analysed by ICP-OES measurements on a Perkin Elmer Optima 7300-DV after complete sample dissolution by mixed acid digestion. To 1 gram of dry sludge, 3 mL of HF and 10 mL of HNO₃ were added in Teflon Parr bomb. The bomb was heated during 4 hours at 180° C. After cooling, the extract was treated with a mix of acid solutions (10 mL HCl, 5 mL HF and 5 mL HNO₃) in presence of H₂O₂ to remove the remaining silicium. The solution was finally dried to 200-250° C to remove HF. Concerning Hg content, the analysis was performed on AMA-254 system of Leco.

RESULTS AND DISCUSSION

Initial Silt Characterization

A systematic characterization of the silt was performed, in order to have the particle size distribution, the elemental composition and the pollutant content.

Particle size distribution

A laser particle size analysis was performed on each silt fraction after mineralurgical treatment of granulometric separation (Table 7). The resulting granulometry is conform to what was expected and compatible with the use of froth flotation for purification of the silt fraction. Nevertheless, it is worth mentioning that S3 is significantly coarser than the other silt fractions S1, S2 and S4.

Table 7 Typical particle size distribution of silt fractions S1 and S2.

	S1	S2	S3	S4
D90 (µm)	58	40	102	50
D50 (µm)	21	14	50	10
D10 (µm)	3	3	7	2

Composition

The major components of the silt fractions are presented in Table 8, as determined by X-Ray Fluorescence, when organic content was estimated by Loss On Ignition (LOI) at 525°C during 2 hours (convention between partners in Solindus project).

The main elements found are silicium, iron, calcium, but with important differences between samples. For instance, Si can vary from 9 to 23 %, Fe from 2 to 20% and Ca from 3 to 12%. From X-Ray diffraction analysis, it is shown that most of the compounds are oxides (SiO₂ quartz, and aluminosilicate for instance) except in the case of calcium which is present under the carbonate form (CaCO₃ calcite). Silt fraction S2 is particular for its high amount of calcite (linked to the dredging location), when S1, S4 and S3 present an increasing amount in iron. Organic content can also vary from 5 to 19%, even if the Solindus mineralurgical treatment used to obtain the silt fraction tends to concentrate the organic matter in the coarser fractions. In that sense S1 is very different from the other sediment.

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Table 8 Silt initial characteristics.

Parameter	Unit	S1	S2	S3	S4
Al	(%)	3.0	2.2	2.5	2.6
Ca	(%)	3.7	12.1	4.3	3.9
Fe	(%)	2.2	1.6	19.5	13.0
K	(%)	0.9	0.7	0.7	1.0
Na	(%)	0.2	0.3	0.3	0.4
Mg	(%)	0.3	0.3	0.6	0.7
Si	(%)	17.8	9.0	18.9	23.3
Organic Matter	(%)	19.4	5.0	10.3	4.7

Pollutant content

Chemical analysis of the heavy metals traces was performed on each silt fraction, knowing that the initial batch of S1 and S2 were only slightly polluted (at intermediate level between class A and B threshold based on the solid analysis, then the need to a complementary leaching test to determine the final class, according to legislation) when S3 and S4 are more polluted (directly into class B due to heavy metals but also PAH content). We observe a concentration of heavy metals, especially Pb and Zn in the corresponding silt fraction obtained after mineralurgical treatment, as expected (Table 9). Initially, all metallic elements requested by the legislation were analyses, but As, Cd and Hg were not problematic in the samples to treat, they will not be mentioned in the rest of the text.

Case encountered for S1 and S2 (first analysis being at intermediate level between threshold A and B) is typical of most of Wallonia dredged matter. When a simple classification step is applied, the choice of the right dimension to operate the separation is a balance to find between the smallest particle size to reach, in order to obtain significant amount in the retained coarse fraction, but with the risk to have passing and retained polluted, and a separation at bigger particle size with the risk not to concentrate enough the volume of polluted material. Further analysis with extra cost and time, is also a common drawback of legislation based on fixed threshold as a rule for pollution classification. Other European countries have a different approach consisting in risk analysis. What is more, the eventual reuse of such fraction as a soil refilling must follow

Table 9 Comparison of pollutant content in the silt fractions with legislation threshold.

	As	Cd	Cr tot (mg/kg of dry matter)	Cu	Hg	Ni	Pb	Zn
Silt S1	25	3	149	97	0.7	56	429	1510
Silt S2	19	6	214	114	0.9	52	500	1368
Silt S3	24	17	165	146	0.5	105	1596	5362
Silt S4	20	7.5	111	42	0.8	36	1909	6586
Class A	50	6	200	150	1.5	75	250	1200
Class B	100	30	460	420	15	300	1500	2400
Threshold*	50	15	165	120	5	210	385	320

* above which a systematic characterisation study is needed, soil refilling (industrial type) [13]

another legislation with other threshold, showing that even non polluted sediment could need a removal treatment especially for Zn: a sediment with Zn concentration below 1200 g/kg of dry matter is considered non polluted, but to be placed in soil with industrial use, Zn content should be below 320 g/kg of dry matter in order to avoid a systematic characterisation study. A similar situation is encountered for total Cr and Cu amount, with respective threshold for non-polluted sediment and industrial soils reuse at 200 and 165 g/kg for total amount of Cr, and 150 and 120 g/kg for Cu content. Currently, Wallonia is revising its legislation in order to harmonize pollutants levels in water, soil and

sediment legislation, increasing the uncertainties about how to interpret the efficiency of the froth flotation treatment.

Laboratory Froth Flotation Tests

For each set of trials (protocols and silt fractions), the analysis of pollutant in the feed, in the total froth recovered, and in the tailings or purified silt are summarized in Table 10.

First protocol P1, based on the use of succinamate, and tested on S1 was giving a stable froth but containing low level of contaminant by visual aspect. On S2, the identical protocol was not leading to any

Table 10 Characteristics of the flotation feed, froth and tailings.

Silt	Protocol		Mass (g)	Cr tot	Cu	Ni (mg/kg)	Pb	Zn
S1	P1	Feed#	822.9	111	92	50	439	1550
		Froth	28.2	120	100	59	625	2028
		Tailings	794.7	111	91	50	432	1533
S1	P1*	Feed#	812.9	93	96	54	397	1411
		Froth	175.4	97	111	68	407	1406
		Tailings	637.5	92	92	50	394	1410
S2	P1*	Feed#	828.4	136	119	52	492	1355
		Froth	166.0	143	155	59	827	1857
		Tailings	662.4	111	110	50	408	1229
S3	P1**	Feed#	551.8	156	135	104	1422	5047
		Froth	154.0	146	141	104	1423	5117
		Tailings	397.8	149	132	104	1418	4497
S4	P1***	Feed#	626.5	214	62	55	1761	6188
		Froth	237.4	359	83	66	2507	6578
		Tailings	389.1	126	15	49	1300	5951
S1	P2	Feed#	844.4	103	103	62	453	1571
		Froth	30.3	95	81	68	379	1575
		Tailings	814.1	103	103	62	450	1455
S2	P2	Feed#	824.8	150	111	52	491	1338
		Froth	65.6	134	192	90	1006	2379
		Tailings	759.2	148	104	50	447	1249
S3	P2*	Feed#	552.7	175	125	113	1198	4328
		Froth	147.3	106	166	86	1578	4910
		Tailings	405.4	173	111	106	1060	4117

Recalculated mean values

stable froth recovery, so no analytical results could be obtained. Then the protocol was adapted by the combination of Sul with Suc, and the replacement of MIBC by PGME (protocol P1*). Those operating conditions were applied to S1 and S2, giving similar results in terms of quality of froth, and with the need to add a fourth flotation step due to high level of contaminants in the froth, as estimated by visual aspect. When applied to S3 and S4, protocol based on Suc/Sul was adapted, (respectively protocol P1** and P1***) with MIBC as frother agent instead of PGME for both, and a significant increase in reagent concentration for P1** applied on S3 and a decrease in reagent concentration for P1*** applied on S4. Visually, quality of froth was poor with S3 and stable with S4. This is why the second protocol, P2, was also tested, first on S1 and S2 using identical conditions, then adapted by adding KEX in combination with KAX (collectors), and replacing PGME by MIBC (frothers, protocol P2*). This last protocol was applied to S4 using identical conditions as S3, but not allowing the formation of a stable froth in that last case.

Considering the amount of froth recovered depending on the protocol used and the silt treated, important differences are observed (Table 10). Indeed, the initial flotation protocol P1 and P2 applied to S1 were generating a thin layer of froth (less than 5%), with low recovery of the pollutant. Adaptation of each protocol was to add a second reagent, sulfonate added to succinamate or ethylxanthate added to amylxanthate. The results of protocol P2 applied to silt fraction S2 were slightly better in the sense that the amount of froth recovered was around 8%, but with a significant increase in the recovery rate of the heavy metals, reaching around 15% for both Zn and lead for example. Further adaptation of the protocols were leading to even higher froth recovery, around 20 % for P1* applied to both sediment slightly polluted S1 and S2, around 27% for the two kinds of protocols applied to S3 (P1** and P2*) and nearly 40% in the case of the last trial (P1***) applied to S4, heavily polluted in Zn and Pb. This shows the difficulty to combine two constraints such as concentrating the pollutant in the smallest amount of froth and removing the highest amount of pollutants.

Knowing that, and in order to estimate the efficiency and the selectivity of the purification step, recovery of element of interest (total Cr, Cu, Ni, Pb and Zn) are plotted on Figure 2, when the corresponding removal rate is plotted on Figure 3. Note that the recovery rate is expressed as the amount of one element recovered in the froth compared to the initial amount of this element in the feed, when the removal rate is expressed as the decrease of concentration of an element in the tailings compared to the initial concentration of this element in the feed.

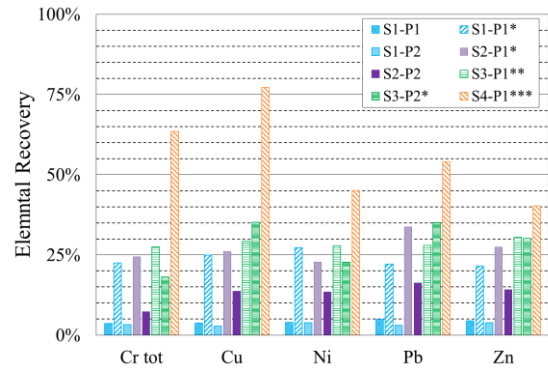


Fig. 2 Comparison of elemental recovery from flotation tests applied to Silt S1-S4.

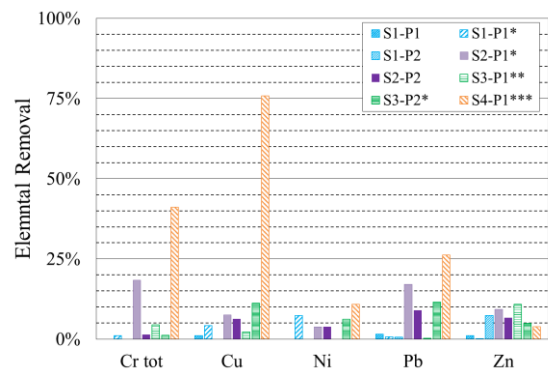


Fig. 3 Comparison of elemental removal from flotation tests applied to Silt S1-S4.

As already indicated by the visual aspect of the froth, results from S1-P1, S1-P2 are very poor regarding either the recovery or the removal rate independently of the kind of protocol used (with or without sulfurization step). The reagent and the conditions used are not allowing a good recollection of the pollutants which remains in the tailings. After adaptation, it is possible to recover a significant amount of Zn and Pb from silt S1, S2 using protocol P1*, even if both of those silt fractions are only slightly polluted. For S1, Pb and Zn recovery can reach 22%, when it is respectively 34% and 27% in the case of S2. This is an important result because the legislation in Wallonia for the reuse of dredged sludge in soil is not the same as the legislation for the classification of such sediment in polluted or non-polluted category (Table 9), with lower threshold level. It is interesting to see that for S2, the protocol using a sulfurizing agent (P2) is giving significant results even if the froth recovery rate was poor (recovery around 15% of Zn and Pb). From the removal rate point of view, similar trends are observed but with lower value, which is not surprising due to the quite low level of contaminant in both silt fractions S1 and S2. Unfortunately, it is not enough at this stage, to allow the use of such silt fraction as soil

refilling material, even for industrial use.

When dealing with more polluted sediment like fraction S3, either flotation based on Suc/Sul reagent or based on KAX/KAX with sulfurizing agent allow to recover significant amount of Zn and Pb, but also Cu, Ni and Cr. The recovery of Zn is around 30% in both cases, when it is slightly better on Pb with KAX/KAX than with Suc/Sul, respectively 35% and 28%. Looking at the removal rate, Suc/Sul protocol P1** seems very selective towards Zn removal compared to protocol KAX/KEX P2*, certainly due to the fact that with the sulfurizing step it not specific to one element, then the collector can more easily react with them all.

Finally, both kind of flotation conditions were also applied to fraction S4, which was even more polluted. Unfortunately, only the protocol using Suc/Sul was efficient, when in the case of KAX/KEX and sulfurizing agent, no stable froth was obtained. This sediment fraction S4 seems very sensitive to the reagent used, and in that case it was possible to recover 40% of Zn and 54% of Pb. High recovery rates are also obtained for the other elements considered: 77% for Cu, 63% for total Cr and 45% for Ni. In the case of the removal rate, we can reach 26% of pollutant reduction in the tailings compared to the feed for Pb, but only 4% for Zn. This protocol P1*** is also efficient for Cu, total Cr and Ni removal, presenting a respective removal rate of 75%, 41% and 11%.

Comparing all those results, it is difficult to extract significant trends regarding the selectivity for removal of lead and zinc because either the nature of the protocol used but also the level of contamination can influence the results. This study shows that, even if it is possible to identify different speciation for the elements to remove in a sample, leading to a theoretical selectivity, the variation in the amount of each pollutant, and the sensitivity of the material to the reagents used and their concentration is so important that no clear trend can be identify so far. The influence of such a great number of parameters regarding the results of flotation could be studied in a more systematic way, as it is already found in the literature [14], showing also that not only the pulp density, pH and collector types are important parameters, but also impeller speed, reagent concentration (collectors and frothers) and airflow rate.

Nevertheless, we have shown here that with the increasing level of contaminant, the selectivity increases slightly, and it was possible to improve successively the operating conditions first by combining two collectors (Suc/Sul or KAX/KEX), then by adapting their concentration. This is putting emphasis on the need to adapt each flotation conditions to the type of matter to be treated, and that there are no reagents families and no operating conditions that can be used universally for Wallonia

sludge. For the scaling up purpose, and since the material is available in sufficient quantity, a trial at pilot scale will be performed in the future, using the two kind of protocol tested here on silt fraction S3 and S4.

We were focused on Pb and Zn removal but it was mentioned earlier that silt fractions S3 and S4 were considered as polluted (class B material) not only due to heavy metals but also due to PAHs. Since it is found in the literature that well-chosen froth flotation conditions can reduce PAHs amount and Cu simultaneously [15], especially when using KAX and MIBC as reagents, in conditions close to P2 protocol series tested here, we will take this point into account for the scaling up tests and perform systematic analysis of both heavy metal and organic pollutant in order to check this effect in the case of Wallonia dredged sediments.

CONCLUSIONS

This study compared the use of the flotation technique to remove heavy metals (especially Pb and Zn) from either slightly contaminated dredged sludge but also highly polluted sediment fractions. Flotation tests were performed on the underflow (-70 +10 µm) obtained from the hydrocycloning of four different Walloon dredge sludge. Two kinds of anionic collectors families were used (combination of Sulfonate (Sul) and Succinamate (Suc) or combination of Amylaxanthate and methylxanthate with sulfurizing agent).

The results were presented in terms of recovery of heavy metals (Pb and Zn mainly, but also total Cr, Cu and Ni) or their removal, depending on the point of view of the metal valorisation or of the purification of the tailings. It shows that either flotation conditions can lead to the partial recovery of elements, even in the case of slightly contaminated sediment, which is of great importance in the actual legislation were the threshold for the reuse of sediment as refilling soils are different and more strict than those for the classification of non-polluted or polluted sediment. When dealing with highly contaminated sediment, it seems that the treated material is very sensitive to the protocol used, as shown by the very good recovery results on S4 with protocol P1*** based on Suc/Sul, when it was not possible to recover stable froth using the same protocol on S3. Then, even the better results (froth recovery of 20 to 30% of the initial feed mass concentrating 27 % to 35% of Zn and Pb recovered in the case of S3) are not sufficient to remove enough contaminant in order to obtain a sediment complying with the soil legislation. Finally, it worth mentioning the extreme case of silt fraction S4, from which it is possible to recover 54% Pb and 40% Zn in the froth concentrating 40% of the initial feed mass when using protocol series based on Succinamate and Sulfonate collectors.

The present promising but not fully satisfactory results give the perspective to transpose at pilot scale (in 750 litres flotation cells) the best protocols of flotation treatment tested here on silt fraction S3 and S4, taking also the opportunity to check removal of heavy metal and PAHs contaminants.

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