Chemical Stabilization Used to Reduce Geogenic Selenium, Molybdenum, Sulfates and Fluorides Mobility in Rocks and Soils from the Parisian Basin

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Abstract: Rocks and soils excavated from civil works frequently present high concentrations of naturally occurring leachable (oxy-)anions. This situation raises concerns regarding the potential transfer of contaminants to groundwater in a storage scenario. This study was carried out to give practical insights on the ability of various stabilizing agents to reduce molybdenum (Mo), selenium (Se), fluorides and sulfates mobility in four types of naturally contaminated excavated materials. Based on standardized leaching tests results, Mo and Se were effectively immobilized after zero valent iron or iron salts additions. Although alkaline materials were found to effectively reduce fluorides and sulfates mobility, their addition occasionally caused a subsequent increase in Mo and Se leaching due to pH increase. None of the reagents tested allowed a simultaneous immobilization of all (oxy-)anions sufficient to reach regulatory threshold values. The remaining difficulties were related to: (i) sulfates leaching from gypsum-rich samples, (ii) fluorides leaching from clayey samples and (iii) Mo and sulfates mobility from tunnel muck. Altogether, the study revealed that the choice of stabilizing agents should be made depending on the speciation of the contaminant or else an opposite impact (i.e., increase in contaminant mobility) might be triggered.

Keywords: geogenic contamination; excavated rocks and soils; chemical stabilization; molybdenum; selenium; fluorides; sulfates; zero valent iron; leaching tests; speciation

Citation: Brandely, M.; Coussy, S.; Blanc-Biscarat, D.; Gourdon, R.; Blanck, G. Chemical Stabilization Used to Reduce Geogenic Selenium, Molybdenum, Sulfates and Fluorides Mobility in Rocks and Soils from the Parisian Basin. *Environments* **2022**, *9*, 78. https://doi.org/10.3390/environments9070078

Academic Editors: Manhattan Lebrun, Domenico Morabito, Lukas Trakal and Sylvain Bourgerie

Received: 15 April 2022
Accepted: 16 June 2022
Published: 25 June 2022

1. Introduction

Leaching of trace elements (TE) from naturally contaminated rocks and soils excavated during land development projects (especially during underground and tunnel construction projects) is now acknowledged as a worldwide issue [1]. With the development of more than 200 km of train lines and 68 new train stations [2], the Grand Paris Express (GPE) project will drastically increase the production of excavated rocks and soils in the Paris area. Objectives have been set to limit the landfilled proportions and promote the reuse of these materials, as long as regulatory constraints are respected. However, some geological formations from the Parisian basin present natural enrichments in TE such as molybdenum (Mo) and selenium (Se) and/or anions such as fluorides (F^-) and sulfates (SO_4^{2-}). Excavated materials transported outside of their construction site have to be considered as waste according to environmental regulations. Their reuse or disposal in one of the three main categories of waste landfills is based on their leaching behavior as stipulated by Annex II [3] of the European Landfill Directive [4]. This regulation has been defined to limit the risk of TE release from stored materials and the subsequent contamination of groundwater. A non-published survey covering more than 900 boreholes from various geological formations

was conducted in the early 2010s over the entire GPE territory. More than 2000 leaching tests were performed on the whole set of collected samples and revealed that Mo, Se, SO_4^{2-} and F^- measured concentrations were above inert waste landfills (IWL) criteria in 15%, 6%, 40% and 9% of the leaching tests, respectively. The transfer of such elements from excavated rocks and soils to the surrounding environment is particularly concerning because of the potential toxic effects associated with overexposure [5–7].

Se and Mo enrichments have been reported in several geological formations of the Parisian basin [8–10]. High Mo contents were mainly found in calcareous formations from Lutetian (Eocene) in which exchangeable fractions could easily overpass 40%wt of total Mo content. In marly limestones, where Mo was assumed to be mainly associated with celestite ($SrSO_4$), leachable amounts were less important but still of concern regarding IWL threshold values [8]. Although sharing similarities with Mo speciation in carbonated excavated materials, highly leachable Se in the Parisian basin was rather observed in clayey rocks and soils from the Ypresian (Eocene inferior) [11,12]. A previous work (under review) focusing on Se speciation in such geological formation suggested that complexation to natural iron (hydr-)oxides played a key role in its mobility over a wide pH range. Like for Mo, associations with sulfated minerals (i.e., celestite) were identified, which was in agreement with studies having investigated the transport of Se from naturally contaminated rocks and sediments [13]. Sulfates leaching from excavated rocks and soils can be explained by the presence of gypsum ($CaSO_4 \cdot 2H_2O$) at concentrations above 0.1%wt, which are likely to induce release above IWL acceptation criteria [14]. Finally, presence of fluorine has been less studied, but preliminary measurements on GPE samples have suggested leached concentrations above IWL threshold values for various geological formations with a particular concern regarding clayey rocks and soils from the Ypresian [15]. The observed high release of fluorides could be explained by fluorite (CaF_2) dissolution or desorption from silicate minerals [16].

The high leachability of (oxy-)anions combined with a relatively low total contents (compared with situations involving anthropogenic inputs) incite the public works company to develop solutions for the management of naturally contaminated materials. Stabilization has been widely studied as a potential in situ or ex situ technique to remediate contaminated soils. However, (oxy-)anions stabilization has received relatively little attention, except in the fields of drinking waters or wastewaters treatments [17–20]. A recent published review reported that among the few articles considering specifically (oxy-)anions, most addressed the remediation of arsenic and chromates contaminated soils [21]. Same observation could be made when focusing on field studies dealing with in situ stabilization of TE contaminated soils [22]. Sulfates and fluorides stabilization in soils was generally considered by the addition of alkaline materials (lime, hydraulic binders, cements . . .) through the incorporation and/or sorption of the anions with the precipitated phases formed (calcium silicate hydrate, CSH; ettringite . . .) [14,23]. Alkaline reactants were also studied to stabilize Se and Mo in artificially contaminated materials [10,24]. Although retention of both oxyanions was reported, the stabilization efficacy could be limited because of competition phenomena [25]. Iron (hydr-)oxides are probably the most widely used stabilizing agents for TE contaminated soils. Interactions between iron (hydr-)oxides and Se or Mo are well documented through basic sorption studies with varying conditions [26–30]. This sorption capacity has been used in Mo/Se contaminated soils using both natural and synthetic oxides (amorphous or crystalline) or iron-based compounds such as iron sulfates ($FeSO_4$) or zero valent iron (ZVI) [31–35]. In most cases, stabilization occurs through sorption and depends on environmental conditions and on iron (hydr-)oxides characteristics. Similar mechanisms are involved when using different kinds of metallic (hydr-)oxides such as aluminum (Al) or manganese (Mn) [27,30]. Other published studies showed that fluorides and sulfates also have affinities with metallic (hydr-)oxides [5,36]. Although other stabilizing agents could be mentioned, the present study focused on alkaline materials, which were widely investigated in soil treatment operations, and metallic-based compounds for their ease of provisioning and relative low-cost.

This paper aims to discuss the impact of these stabilizing agents on Mo, Se, sulfates and fluorides mobility in four naturally contaminated materials excavated during GPE construction sites. The materials were chosen because they all showed a concerning mobility regarding at least one of the aforementioned (oxy-)anions. Geogenic contamination is raising more and more concerns and yet, only few studies exist on TE fates after excavation as well as on potential treatment solutions. To fill this gap, stabilization efficiency, which was defined as the ability of a given stabilizing agent to reduce contaminants mobility below the IWL acceptation criteria, was assessed by comparison between results of standardized batch leaching tests (SBLT) carried out on raw and stabilized samples. This experimental approach allowed us to evaluate the short-term performance of stabilization to select the reagents likely to be further considered in long-term studies. Moreover, given the disparity of behavior and composition of excavated materials, the influence of their characteristics on stabilization efficiency was investigated with a particular emphasis on leachable elements initial speciation influence.

2. Materials and Methods

2.1. Excavated Rocks and Soils

Four samples of excavated rocks were collected from GPE construction sites. After sampling, the materials were stored at ambient temperature in plastic bags. A complete characterization of the studied materials was realized during previous work [8], so that their main mineralogical and chemical characteristics could be listed in Table 1, while their origins and natures are summarized below:

- A calcareous sample (CS) mainly composed of carbonates from the Eocene period (Lutetian inferior, (depth. 24–27 m)) was collected by a mechanical excavator in Courbevoie (Hauts-de-Seine, France) in March 2018.
- A marly limestone sample (MLS-A) was extracted in Vitry-Sur-Seine (Val-de-Marne, France) in March 2018 and corresponded to sulfate rich carbonates from the Eocene period (Lutetian superior, (depth. 13–14 m)).
- A loamy sample (LS) was collected in Clamart (Hauts de Seine, France) in November 2018. It was mainly composed of clayey minerals from the Eocene period (Ypresian inferior, (depth. C.a. 15 m)).
- A tunnel muck sample I was extracted by a tunnel-boring machine below the city of Vitry-sur-Seine (Val-de-Marne, France). Its digging horizon was at the border between CS and MLS-A geological formations (depth. 30–40 m). This material followed several steps of treatment carried out directly in a slurry treatment plan located on the construction site. In particular, lime was added to the slurry to facilitate subsequent de-watering operations.

2.2. Reagents

Reagents described below were used on two of the four samples to evaluate their ability to reduce Mo, Se and F^- release in priority. CS and LS were chosen because preliminary leaching tests on raw materials showed the highest mobility for Mo and for Se and F^-, respectively. Then, a short-list of reagents was tested on two other samples (MLS-A and TM) to assess their impact on (oxy-)anions mobility when applied to different geological formations containing high levels of sulfates. Table 2 presents a summary of all stabilizing treatments having been applied to each sample as well as the number of replicates involved.

Table 1. Overview of raw excavated materials main characteristics as defined in previous work [8]. A scale for (oxy-)anions mobility commonly observed in each sample is proposed based on SBLT results: (−) weak mobility systematically below IWL acceptation criteria; (+) slight mobility with occasional overrun of IWL acceptation criteria; (++) strong mobility systematically above IWL acceptation criteria; (+++) highly concerning mobility leading to evacuation in more constraining waste landfills.

Sample	Geological Formation	Excavation Site	Main Characteristics	Natural pH	(oxy-)anions Mobility	Trace Elements Speciation
CS	Lutetian Limestone (Eocene, Lutetian inferior)	Courbevoie	Almost exclusively composed of carbonated minerals (mainly calcite)	8.8	Mo +++ Se + SO_4^{2-} − F^- +	Mo mainly exchangeable and presenting associations with pyrites and carbonated minerals Se exchangeable fraction at pH_{nat} only represent 5% of total Se
MLS-A	Lutetian Marly Limestones (Eocene, Lutetian superior)	Vitry-Sur-Seine	Mainly carbonated (calcite, dolomite) with high content of sulfates (gypsum, celestite)	7.6	Mo ++ Se + SO_4^{2-} +++ F^- +	Mo and Se mainly associated with celestite TE exchangeable fractions represent 10%wt of total TE
LS	Ypresian Clays (Eocene, Ypresian inferior)	Clamart	Mainly composed of clay minerals (smectite and kalonite) Presence of natural oxides (Ti, Fe)	8.0	Mo − Se +++ SO_4^{2-} − F^- +++	Mo almost exclusively insoluble Se mainly exchangeable with equal repartition between Se_{VI} and Se_{IV}, the former being retained at oxides' surfaces at pH_{nat}
TM	Lutetian Limestone and Lutetian Marly Limestones	Vitry-Sur-Seine	Mainly carbonated (calcite, dolomite) Presence of sulfate (gypsum, celestite) Composition impacted by liming carried out after excavation (precipitation of ettringite, partial dissolution of celestite, Mo impoverishment)	12.2	Mo +++ Se − SO_4^{2-} ++ F^- +	Mo highly exchangeable with small incorporation in ettringite and associations with celestite, carbonated minerals and pyrite Se mostly insoluble with similar associations

SBLT = Standardized batch leaching tests; IWL = Inert wastes landfill; pH_{nat} = the natural pH of soils.

Table 2. Summary of the treatment (stabilizing agent + dosage) tested for each excavated material. For each case, the number of replicates used is indicated. When a dash is mentioned, the corresponding treatment has not been tested.

Treatment	CS	LS	MLS-A	TM
Raw Sample	**9**	**7**	**6**	**6**
Zero valent iron (ZVI)				
1%	4	2	2	1
2%	4	-	1	1
3%	4	2	1	1
Iron sulfate ($FeSO_4$)				
1%	3	2	-	-
2%	2	-	-	-
3%	2	2	-	-
Aluminum hydroxide ($Al(OH)_3$)				
1%	2	2	1	1
2%	2	-	-	1
3%	4	2	-	1
Magnetite (Fe_3O_4)				
1%	2	2	2	-
2%	2	-	2	-
3%	2	2	-	-

Table 2. *Cont.*

Treatment	CS	LS	MLS-A	TM
Raw Sample	**9**	**7**	**6**	**6**
Hematite (Fe_2O_3)				
1%	2	2	2	-
2%	2	-	2	-
3%	2	2	-	-
Manganite (MnOOH)				
1%	2	2	2	-
2%	2	-	2	-
3%	2	2	-	-
4%	1	-	-	-
Lime (CaO)				
1%	2	-	-	1
2%	-	2	1	1
4%	2	2	1	1
Calcium sulfoaluminate clinker (CSA)				
2%	4	4	-	-
3%	-	-	-	2
4%	3	4	-	-
Portland cement + lime (PC/CaO)				
1%	1	-	2	1
2%	-	5	-	1
4%	8	5	-	1

The stabilizing reagents tested were either natural (hydr-)oxides: magnetite (Fe_3O_4), hematite (Fe_2O_3) and manganite (MnO(OH) or synthetic materials: Al hydroxides (Acros Organics, >99%), iron sulfates ($FeSO_4$) (VWR, >99%) and zero valent iron (ZVI) (VWR, >98%). Alkaline materials were also tested for stabilization. They were selected from the reagent materials classically used for soil treatments: lime (CaO), calcium sulfoaluminate clinker (CSA) and a hydraulic binder (PC/CaO) mainly composed of Portland cement with high lime content (>30%).

2.3. Stabilization Protocol

Stabilization treatment was performed by mechanical mixing using a cutting mixer during approximatively 5 min. This duration was long enough to obtain a good homogeneity of the mixture except for LS where manual breaking of clayey blocks and a longer period of mechanical mixing were needed. The mass of stabilizing agent to add, m_{stab}, was calculated using Equation (1) to obtain the targeted mass percentage (W):

$$m_{stab} = \frac{W \times (m_{sol} \times DMC)}{1 - W} \quad (1)$$

where m_{sol} is the quantity of excavated material to stabilize and DMC is the Dry Matter Content.

Curing period, which represents the time between stabilizing agent addition and standardized batch leaching tests (SBLT), was set to 5 days to account for the necessity of obtaining a fast immobilization of labile elements.

2.4. Standardized Batch Leaching Tests

SBLT were carried out on raw samples and on the mixtures obtained after the stabilization treatments according to a standardized protocol [37]. Raw and treated samples were crushed (<4 mm), dried (38 °C) and contacted with water at a liquid/solid (L/S) ratio of 10 $mL \cdot g^{-1}$ for 24 h in an end-to-end agitator. pH of the eluates was measured and supernatants were analyzed after centrifugation (30 min, 2000× g) and filtration (<0.45 µm). Leached concentrations of Mo and Se were determined by ICP-MS while F^-

and SO_4^{2-} were analyzed with potentiometric [38] and spectrophotometric UV/vis [39] detection, respectively.

3. Results

Figures 1–4 show SBLT results obtained for each excavated material in the form of graphs, plotting leached concentrations of monitored elements as a function of pH for raw and stabilized agents. Detailed analytical results on each stabilized sample are presented in Supplementary Materials (Tables S1–S4).

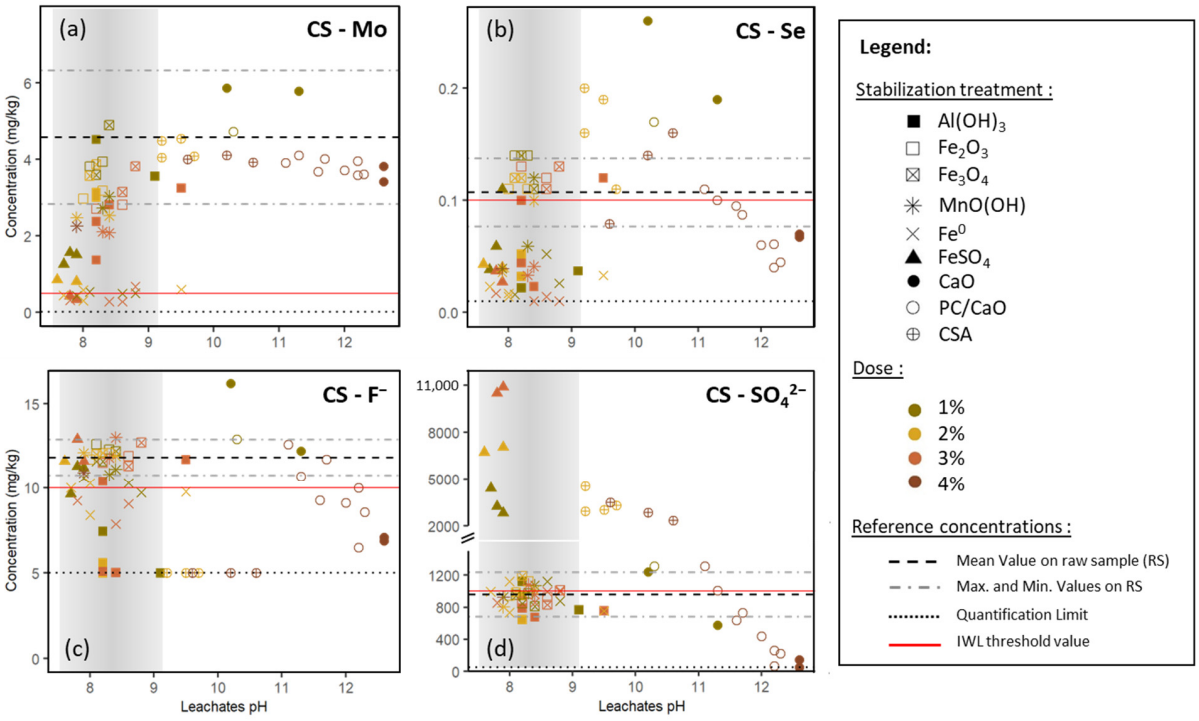

Figure 1. Mo (**a**), Se (**b**), fluorides (**c**) and sulfates (**d**) concentrations in the leachates of standardized leaching tests as a function of pH and of the stabilizing treatment in CS. Vertical gray areas represent the samples commonly observed natural pH. Attention has to be paid on the gap in the *y*-axis of CS-SO_4^{2-} (**d**).

3.1. Calcareous Sample

Se and more particularly Mo were released above inert wastes landfill (IWL) threshold limits (0.5 and 0.1 $mg{\cdot}kg^{-1}$ for Mo and Se, respectively). Overall, their leached concentrations were modified in a similar manner by the different stabilizing agents, but some specificities were observed. First, Mo and Se leaching was strongly reduced by the treatment with ZVI (Figure 1a,b) down to leached concentrations almost systematically below IWL limits. The leaching of both elements was also strongly reduced by the treatment with $FeSO_4$, below IWL limits using a 3%wt amendment ratio. The use of oxides as stabilizing agents was less effective. Fe oxides did not affect Mo mobility and seemed to slightly enhance Se release. The use of Al and Mn oxides allowed reducing Se leached concentrations below IWL limits in most of the SBLT carried out (Figure 1b). However, although also reduced, Mo leaching was still systematically above IWL acceptation criteria (Figure 1a). The main difference between Se and Mo behavior in stabilized CS was observed when pH was increased. On one hand, Mo released concentrations were not significantly influenced by lime, CSA or PC/CaO additions (Figure 1a). On the other hand, Se leached concentrations were strongly pH dependent (Figure 1b). While the leached concentrations were higher from stabilized than raw samples at pH values between 9 and 11, the opposite

was observed at pH > 11. Se mobility was even further reduced by a factor 2 and more at the highest pH values.

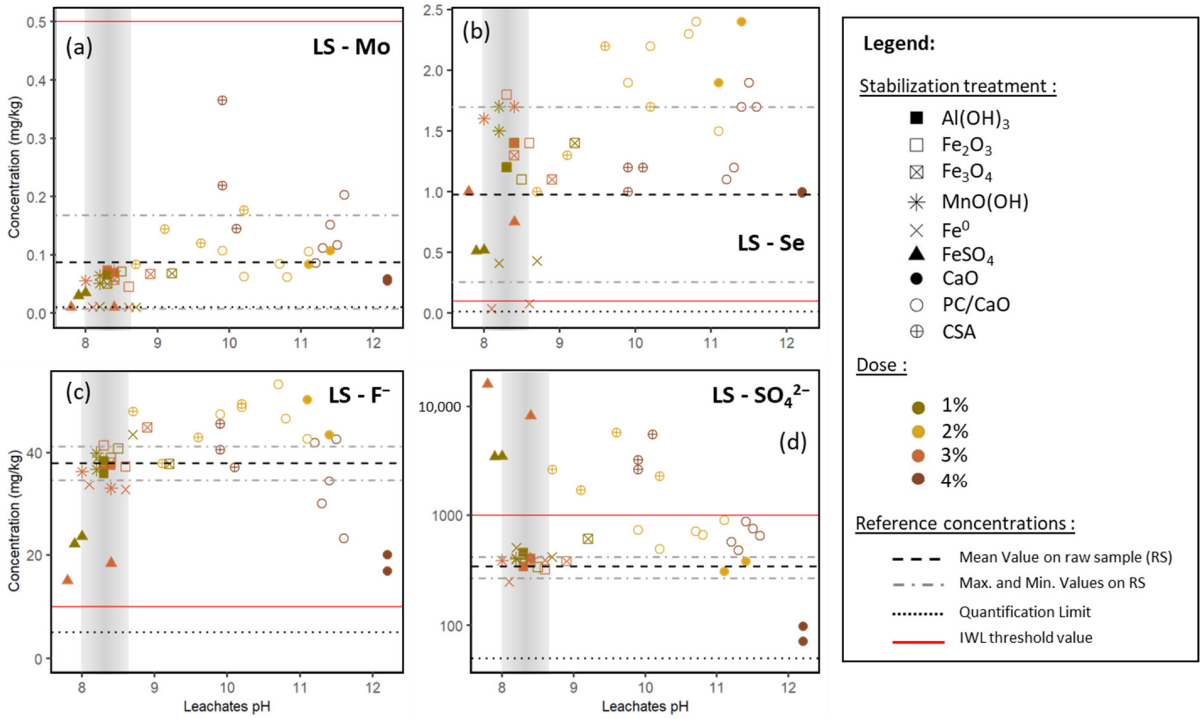

Figure 2. Mo (**a**), Se (**b**), fluorides (**c**) and sulfates (**d**) concentrations in the leachates of standardized leaching tests as a function of pH and of the stabilizing treatment in LS. Vertical gray areas represent the samples commonly observed natural pH. Attention has to be paid on the logarithm scale for LS-SO_4^{2-} (**d**).

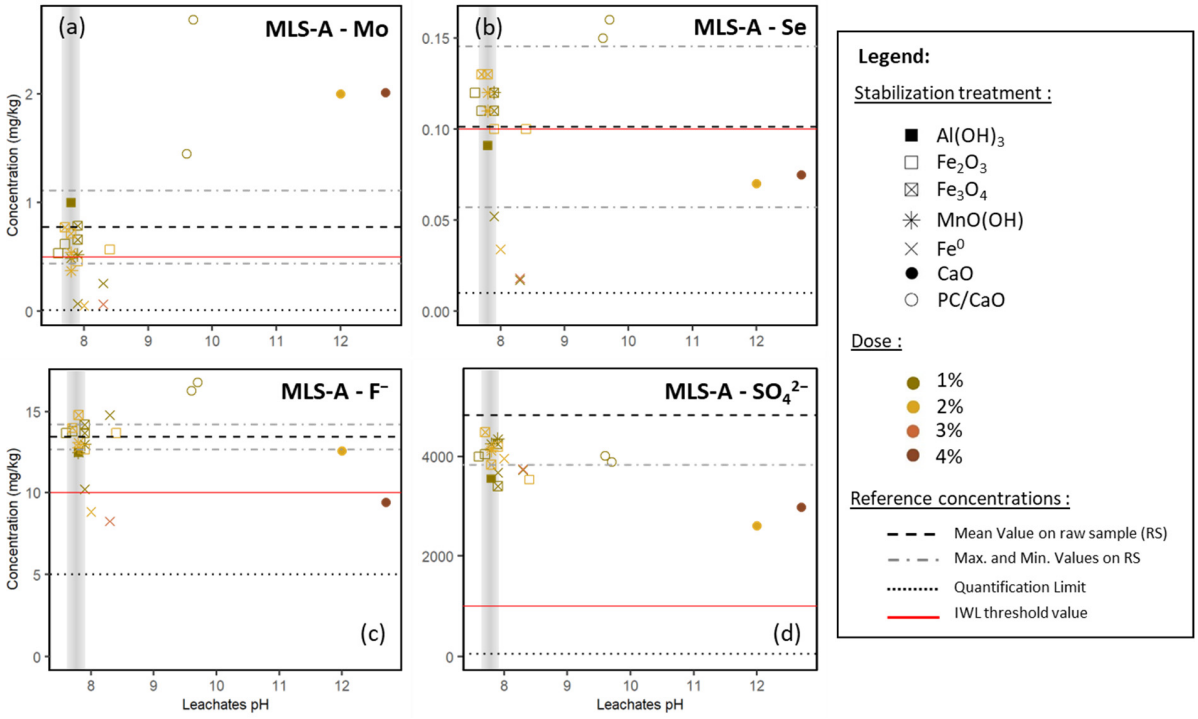

Figure 3. Mo (**a**), Se (**b**), fluorides (**c**) and sulfates (**d**) concentrations in the leachates of standardized leaching tests as a function of pH and of the stabilizing treatment in MLS-A. Vertical gray areas represent the samples commonly observed natural pH.

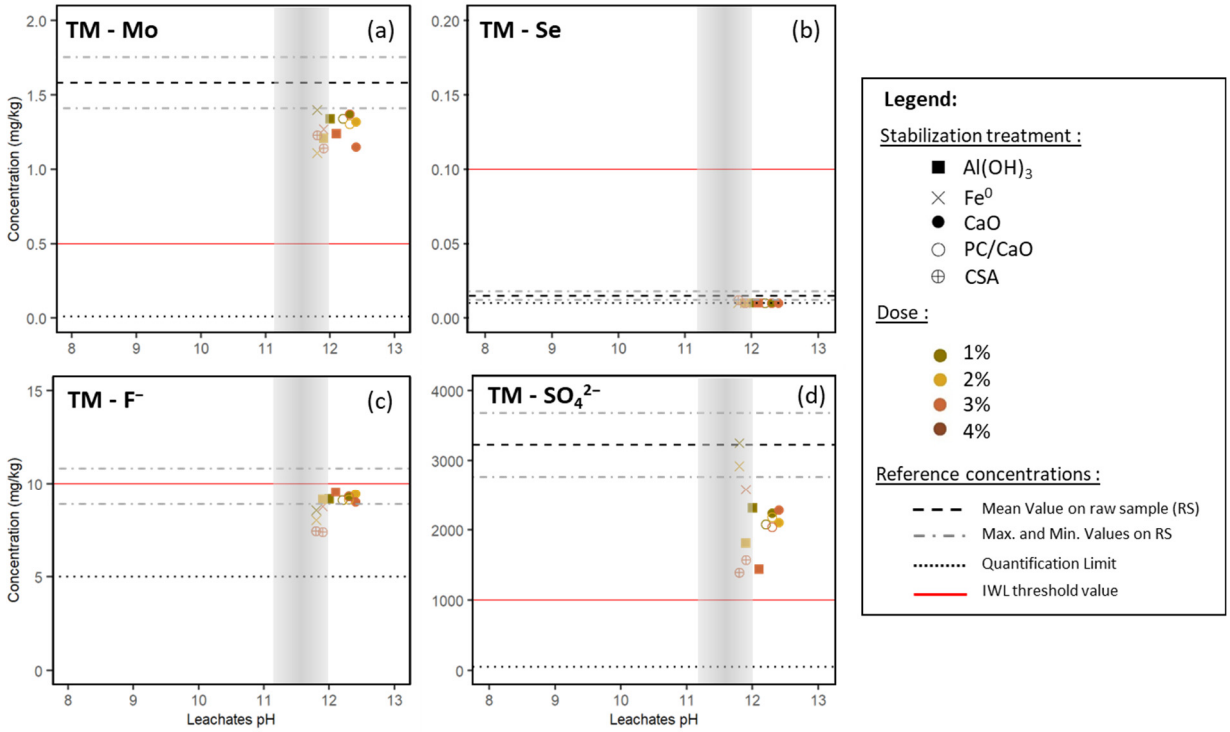

Figure 4. Mo (**a**), Se (**b**), fluorides (**c**) and sulfates (**d**) concentrations in the leachates of standardized leaching tests as a function of pH and of the stabilizing treatment in TM. Vertical gray areas represent the samples commonly observed natural pH. Dashed and dot dashed horizontal lines represent the mean value and the extrema values observed on raw sample. Red solid lines represent inert wastes landfill (IWL) acceptation criteria and dotted lines the limit of quantification.

Fluoride's mobility in the raw sample was slightly above IWL limit (10 mg·kg^{-1}). Treatments with ZVI and Al oxides were found to reduce only slightly fluorides leaching, while a stronger decrease was observed with CSA material, which systematically led to leached concentrations below the QL (5 mg·kg^{-1}) (Figure 1c). Fluoride's mobility was also significantly reduced with the use of PC/CaO and lime but only for pH values above 11 (as noticed for Se). This trend was also observed for sulfates stabilization (Figure 1d), which was only efficient using lime or PC/CaO at pH above 11.5. All other stabilizing agents were ineffective to reduce SO_4^{2-} mobility, which remained close IWL limit (1000 mg·kg^{-1}). The use of sulfate bearing materials as stabilizing agents even resulted in a strong increase in SO_4^{2-} release.

3.2. Loamy Sample

In LS, ZVI reduced Se leaching only when used at concentrations of 3%wt and more (Figure 2b). It was the only stabilizing agent to decrease leached concentrations below IWL limits. Using $FeSO_4$ or ZVM reduced leaching only slightly, while metallic oxides did not significantly affect Se release (leached concentration between the mean and the maximum values observed in raw samples). With pH increase, Se release was further enhanced, especially when using small amounts of stabilizing agents (i.e., 2%wt of lime, CSA or PC/CAO). For higher dosages (i.e., 4%wt), Se leaching concentrations were close to the mean value observed in the raw sample, suggesting that the negative effect of pH increase was somehow compensated. Mo release from unstabilized LS was always below IWL limits and even occasionally below QL. It can be noted that when using a stabilizing agent which has a limited impact on pH (i.e., ZVI, oxides, $FeSO_4$ . . .), the leached concentrations remained below the mean value observed in the raw sample, while pH increase induced higher leached concentrations (Figure 2a). Fluorides were highly leachable in LS and most of the stabilizing agents used had little effect on their release (Figure 2c). $FeSO_4$ and lime or

PC/CaO at high dosages (with pH > 11) divided by 2 fluorides leaching concentrations, which, however, remained above IWL limits. ZVI addition was almost ineffective. When pH was buffered between pH = 9 and 11 by addition of lime, CSA or PC/CaO, the trend was clearly an increase in fluorides leaching. Finally, LS was the only material for which sulfates leaching was not of concern given the absence of sulfated minerals in this sample (Figure 2d).

3.3. Marly Limestone Sample

Only six stabilizing agents were tested for MLS-A. ZVI was found to reduce Mo leaching below IWL limits. Mn oxides also reduced Mo leaching but to concentrations close to the threshold value (Figure 3a). Other oxides (Al and Fe) did not have any effect. The increase in pH following the addition of lime or PC/CaO increased leached Mo concentrations by a factor 2 and more. The same effects were observed on Se leaching, excepted at high pH. Indeed, at pH >10, Se leached concentrations remained below the mean value observed on raw sample and were not further increased as observed at pH between 9 and 10 (Figure 3b). Dosages of at least 2%wt of ZVI were needed to reduce fluorides leached concentrations below (but close to) IWL limit (Figure 3c). Here again, oxides had no particular effects and pH between 9 and 10 led to further increase in F^- leaching. Sulfates were released in high concentrations from MLS-A mainly because of gypsum presence. A significant reduction in sulfates leaching was achieved only when using lime. The resulting leached concentrations were above IWL threshold value (Figure 3d) but below the threshold limit for non-dangerous wastes landfill (NDWL) of 3000 $mg \cdot kg^{-1}$.

3.4. Tunnel Muck

Five stabilizing agents were tested on this sample (ZVI, Al oxides, CSA, PC/CaO and lime). Although a small reduction in Mo and F^- leaching was observed with all the reagents, the effect was very low (Figure 4a,c). A more significant decrease was observed for sulfates leaching but leached concentrations remained above IWL limit. The efficiency of the stabilizing agents ranged as follows: CSA > Al oxides > lime = PC/CaO > ZVI (Figure 4d).

4. Discussion

4.1. Effect of Metal Based Reagents

The efficiency of metal oxides to reduce TE mobility strongly depends on parameters such as pH, oxide type and competition between ions [40]. Under oxic conditions, Mo and Se are likely to be found under their oxyanionic forms (molybdate MoO_4^{2-}; selenite SeO_3^{2-} and selenate SeO_4^{2-}) [41,42]. Adsorption would then be favored at acidic pH, where oxide surface sites are mainly positively charged [43]. Hence, the slight (CS, LS and MLS-A) to strong (TM) alkaline pH occurring in the studied excavated materials could explain why all (hydr-)oxides used here (Fe, Al or Mn) had only a small impact on Mo and Se leaching behavior. Although sulfates were not expected to have a strong competitive effect on Mo adsorption at oxide surface sites [44], their presence at very high levels (especially in MLS-A) might have prevented TE immobilization by limiting the available number of surface sites. Competition for adsorption sites could also occur with (bi)-carbonate ions [45] in the predominantly carbonated samples (CS and MLS-A). The use of iron oxides precursors (ZVI and iron salts) led to a significant decrease in Mo and Se mobility in CS, MLS-A and LS whereas it was ineffective in the case of TM because of the high pH due to liming after material excavation. Oxidation of zero-valent iron along with $FeSO_4$ decomposition were expected to produce amorphous iron (hydr-)oxides [46]. Using iron sulfates, precipitation would result in sulfuric acid (H_2SO_4) production, which, although not having a significant impact on pH because of carbonates buffering capacity, would eventually enhance protonation of oxide surface sites. Hence, (oxy-)anions complexation might be favored compared to direct iron (hydr-)oxides amendments. In addition, it can be noted that, at the same dosage of stabilizing agent, ZVI had the advantage to

present a higher proportion of Fe compared to iron (hydr-)oxides or salts [46]. Hence, the sink for oxides precipitation was larger and would eventually lead to the creation of a more important number of surface reactive sites. Long-term efficacy of stabilization might also benefit from the fact that ZVI oxidation was kinetically limited and fresh amorphous iron (hydr-)oxides would be produced over a longer period of time as compared to $FeSO_4$ [46]. The higher efficacy of ZVI or $FeSO_4$ compared to iron oxides could also be linked to the formation of amorphous oxides such as ferrihydrite ($Fe(OH)_3$). Indeed, such poorly crystalline mineral phases are known to have a larger specific surface area [47], which is expected to favor complexation phenomena compared to crystalline iron oxides. Finally, ZVI could both induce oxidation or reduction reactions through the release of Fe(II) species [48,49]. The significant Se immobilization observed in LS and CS with ZVI amendments was not consistent with an oxidation path, which would disadvantage complexation at the excavated materials natural pH. Hence, ZVI might be assumed to act as a reductant and to some extent convert the highly leachable selenate (SeO_4^{2-}) ion into a selenite (SeO_3^{2-}) ion, which would be more likely to adsorb at alkaline pH [50]. Se reduction is a stepwise reaction, which might eventually lead to the production of insoluble elemental selenium (Se_0) and/or selenides (Se_{-II}). However, this path was mostly acknowledged for Se removal from solutions during batch experiments [18,51] and no evidence has been found in a context of low contaminated excavated materials stabilization.

Sulfates leaching was not significantly modified in CS and LS, where the sink of leachable sulfates was initially low. On the other hand, the leaching was more reduced in MLS-A, where sulfates were initially highly leachable. However, the stabilization effect remained relatively low with leached concentrations from stabilized samples never lower than the lowest value observed on raw samples. These results suggested that sulfur total content (especially gypsum) in MLS-A was simply too high to be immobilized by complexation onto oxide surfaces using reasonable dosages (up to 3%wt) of metal-based reagents. Interestingly, it was observed that sulfates leaching was reduced in TM by the addition of Al (hydr-)oxides. Given the alkaline pH of this material, complexation was probably not the stabilizing mechanism, which more likely occurred through the precipitation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O$). Indeed, the instability of Al (hydr-)oxides in pH regions over 10 would result in Al release [52]. Yet, the presence of Al was the limiting factor for ettringite precipitation in TM since all other conditions were gathered (i.e., pH > 10 due to liming, available Ca due to carbonated minerals and liming and available sulfates due to gypsum and celestite) [53]. Such a mechanism was consistent with experimental observations since the highest dosage of Al oxides led to the lowest sulfates release.

Fluorides release was reduced by ZVI, $FeSO_4$ and Al (hydr-)oxides amendments in CS, and by ZVI in MLS-A, which could probably be attributed to complexation under the slightly alkaline conditions observed [17]. Quantitatively, the additions of ZVI and $FeSO_4$ led to a higher stabilization of fluorides in LS as compared to CS. Since immobilization mechanisms were expected to be identical, this observation suggested different fluorides initial speciations in the samples, due to the different characteristics of the excavated materials. In LS, the presence of smectite in large amounts might be a sink for exchangeable fluorides, which are known to interact weakly with clay minerals surface sites [54]. On the other hand, in carbonated materials such as CS, fluorides might rather be present as calcium fluorides (CaF_2), which are poorly soluble under near-neutral conditions and low temperatures [55]. Therefore, the higher proportion of exchangeable fluorides in LS as compared to CS would explain their higher stabilization observed in LS by the addition of metal-based reagents.

Figure 5 allows a direct visualization of ZVI impact on Mo, Se, F and SO_4^{2-} mobility as a function of the quantity added for each sample. The relative inefficiency acknowledged for sulfates and fluorides in all samples as well as for Mo in TM is confirmed here. One can see a difference between Mo stabilization in CS and MLS-A, which was significant with the smallest addition of ZVI (1%wt), and Se stabilization in LS, for which a 3%wt

amendment was necessary to reduce Se leaching below IWL acceptation criteria. This might be a consequence of the slightly different mechanisms mentioned before. The exchangeable Mo was expected to be present in a MoO_4^{2-} form easily adsorbed by the freshly formed iron (hydr-)oxydes. On the other hand, exchangeable Se in LS was expected to be split between its SeO_4^{2-} and SeO_3^{2-} forms. Hence, the adsorption through weak interactions of SeO_4^{2-} and/or its reduction into SeO_3^{2-} might have needed higher concentrations of ZVI.

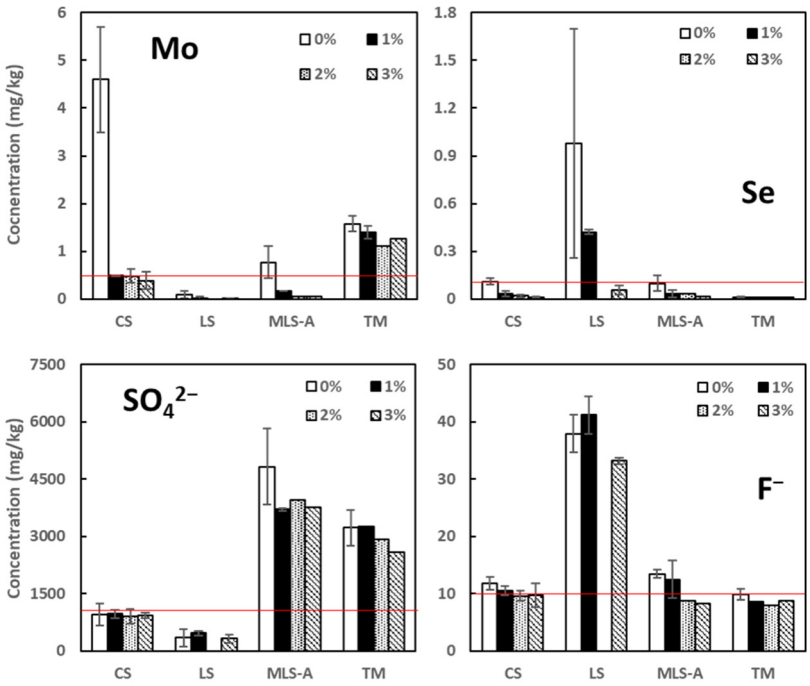

Figure 5. Concentrations of Mo, Se, sulfates and fluorides in the leachates of batch leaching tests [37] as impacted by the percentage of zero valent iron added in CS, LS, MLS-A and TM. If no bars are presented for a given percentage, then this percentage has not been tested for the sample concerned. Red horizontal lines refer to the IWL threshold value.

4.2. Effects of Alkaline Reagents

The addition of PC/CaO and lime was observed to increase pH above 10 whereas CSA addition increased pH less strongly to values between 9 and 10. As a result, F^- and SO_4^{2-} leaching was reduced here by alkaline reagents except for sulfates with CSA amendments. At pH above 11, where ettringite precipitation was favored, leached concentrations of sulfates were reduced below the lowest value observed on raw carbonated samples (CS, MLS-A and TM). In LS, however, no significant decrease was observed in sulfates leached concentrations after lime or PC/CaO addition, suggesting that ettringite did not precipitate due to relative scarcity of sulfates. On the other hand, under the same conditions (pH > 11) a decrease in fluorides leaching was observed with all excavated materials, including LS. Although fluorides incorporation in ettringite was reported in some studies dealing with fluorides removal from water using wastes materials [23], this phenomenon was unlikely to occur in LS. Thus, precipitation of calcium fluorides (CaF_2) [5] and/or interactions with CSH might rather be considered as the main stabilizing mechanisms. Under slightly lower pH values (between 9 and 10), higher fluorides leached concentrations were observed, probably due to the combined effect of a slight undersaturation of initial bearing minerals (fluorite) and unfavorable conditions for F^- complexation. At such pH values, both effects were not compensated by F^- incorporation in ettringite or adsorption onto CSH. Finally, one can note that the slurry treatment preceding TM sampling involved addition of lime so that ettringite precipitation might already have reached equilibrium. Hence, the use of lime as a stabilizing agent in TM induced only a small reduction in sulfates leaching. On the

other hand, provisioning the system with Al (through sulfoaluminate CSA addition) further enhanced ettringite formation, leading to a slightly stronger stabilization (Figure 4c,d).

It has been reported that the stabilization of oxyanions can occur by substitution of sulfates by selenate and/or molybdate ions in ettringite structure during its precipitation [25]. Hence, Se and Mo concentrations would be expected to decrease with pH increase especially above 11. This phenomenon was observed here only in CS (Figure 1a,b), suggesting that in this sample both oxyanions were mainly exchangeable and readily available for incorporation into ettringite. Selenium was relatively more incorporated than Mo, which was consistent with the interaction preferences reviewed by [25]. In MLS-A, Se was poorly affected while Mo concentrations in the leachates strongly increased with pH, which was radically different from the observations made on CS. This result may be attributed to the initial speciations of these elements in MLS-A, where celestite was the main Mo-bearing phase. In a previous work [8], the authors observed that the addition of sodium hydroxide (NaOH) to MLS-A induced similar evolution patterns of Mo leached concentrations under alkaline pH. It was shown by geochemical modelling and scanning electron microscopy coupled with electron probe microanalysis (SEM-EPMA) that the phenomenon was explained by the partial dissolution of celestite. Although celestite was suspected to bear a small quantity of selenium as well, Se exchangeable fraction was proportionally higher as compared to Mo. Since Se incorporation in ettringite was favored, it was considered that the mechanism of stabilization was compensated by celestite dissolution, resulting in the globally unchanged leached concentrations observed (Figure 3b). Finally, for LS, Mo and Se release was increased by the addition of alkaline materials, revealing their poor sorption onto natural oxide surface sites. Indeed, a previous study (results not shown) addressing Se speciation in LS had inferred that, at material natural pH, almost one third of total Se was retained through inner-sphere complexation of selenite onto natural iron oxides. Furthermore, since ettringite precipitation was unlikely to occur in this sample, no stabilizing effect of alkaline material was observed. Hence, even the highest dosage of lime tested here did not succeed in significantly reducing TE leaching.

5. Conclusions

Metal-based compounds and alkaline reagents were investigated for their capacity to reduce the leaching of anions and oxyanions (fluorides, sulfates, Mo and Se) from four rock materials representing (oxy-)anions mobility issues of the Grand Paris Express (GPE) project. Results from standard leaching tests showed that none of the stabilizing agents tested were able to reduce simultaneously the leaching of all considered (oxy-)anions to comply with inert wastes landfill threshold values. Nevertheless, zero valent iron was identified as a promising reagent to control Mo and Se release through adsorption onto oxide surfaces. A decrease in fluorides and sulfates leaching was also observed, but the stabilization effect was not sufficient when applied to the excavated materials with the highest initial leachability. Conversely, alkaline materials, particularly PC/CaO and lime, were found to efficiently reduce the leaching of sulfates and fluorides but were unsuccessful in TE stabilization due to pH increase. In particular, it was found that alkaline reagents induced an undesirable increase in leaching when applied on TE-bearing celestite rich materials, due to $SrSO_4$ partial dissolution.

Little is known on the behavior of (oxy-)anions in naturally contaminated rocks and soils, which complicate their disposal and the management of the associated environmental risk. Overall, this study showed that metallic-based reagents (especially ZVI) could be considered as an efficient stabilizing reagent in materials showing mobility issues restricted to TE (i.e., Mo and Se). Nevertheless, to ensure the reliability of chemical stabilization used on naturally contaminated rocks and soils, the long-term efficiency of the solution should be addressed in future works.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/environments9070078/s1, Table S1: Results of standardized leaching tests (NF EN 12457-2) carried out on CS using various stabilizing agents; Table S2: Results of standardized leaching tests (NF EN 12457-2) carried out on LS using various stabilizing agents; Table S3: Results of standardized leaching tests (NF EN 12457-2) carried out on MLS-A using various stabilizing agents; Table S4: Results of standardized leaching tests (NF EN 12457-2) carried out on TM using various stabilizing agents.

Author Contributions: Conceptualization, M.B. and S.C.; Funding acquisition, S.C.; Investigation, M.B. and S.C.; Methodology, M.B. and S.C.; Project administration, S.C.; Resources, M.B. and G.B.; Supervision, S.C., D.B.-B. and R.G. Writing—original draft, M.B.; Writing—review and editing, S.C., Denise Blanc-Biscarat, Remy Gourdon and G.B. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been financially supported by Bouygues Travaux Publics (France) as a part of IMMOTERRE research and development project.

Data Availability Statement: Raw data of standardized batch leaching tests are available in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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