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Adrien Cabrerizo, David Bulteel, Julien Waligora, Gautier Landrot, Emiliano Fonda, et al.. Chemical, mineralogical, and environmental characterization of tunnel boring muds for their valorization in road construction: a focus on molybdenum characterization. *Environmental Science and Pollution Research*, 2020, 27 (35), pp.44314-44324. 10.1007/s11356-020-09969-6 . hal-03224416

HAL Id: hal-03224416

<https://hal.science/hal-03224416>

Submitted on 5 Jul 2021

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Chemical, mineralogical, and environmental characterization of tunnel boring muds for their valorization in road construction: a focus on molybdenum characterization

Adrien Cabrerizo¹  · David Bulteel¹ · Julien Waligora² · Gautier Landrot³ · Emiliano Fonda³ · François Olard²

Abstract

Tunnel boring muds, coming from underground works, are considered as specific materials due to their intrinsic characteristics (granularity, clay content, water content, presence of heavy metals). In order to determine if they can be valorized in road construction or civil engineering, a complete characterization, including their environmental behavior, is necessary. Thus, the aim of this study is to characterize a tunnel boring mud sample from chemical, mineralogical, and environmental point of view. The studied material, a limestone mud, was characterized using different analytical techniques. Some pollutants and heavy metals were identified, such as sulfates and molybdenum (Mo), and specific analyses were performed to identify molybdenum speciation. As molybdenum was detected as traces in the studied material, it was necessary to increase its concentration. Thus, a nitric acid extraction was specifically developed at a laboratory scale with the aim to remove its high-calcium carbonate content. Then, synchrotron analyses were performed, allowing to obtain data on the oxidation state of molybdenum.

Keywords Tunnel boring mud; Environmental characterization; Molybdenum speciation; Extraction method

Introduction

Grand Paris Express is the largest transport project in Europe. It consists in a fundamental rethink, redesign, and focus on the public transport network on the scale of the metropolitan area. Grand Paris Express also involves the extension of existing metro lines, and this project will require the use of a significant number of tunnel boring machines (TBM). These development works will generate an estimated 45 million tons of excavated polluted materials (muds) within the next 10 years (Société du Grand Paris 2017).

Tunnel construction requires careful consideration of the management of excavated materials insofar as it involves environmental, economic, logistic, and legal requirements. Excavated materials could be valorized in civil engineering (Bellopede and Marini 2011; CETU 2016; Colas 2012; Descoedres et al. 2006) and especially in road construction that needs large amounts of materials each year. Such a valorization allows to preserve natural resources, reduce transport impacts, and propose alternative technical solutions, switching from a linear production model (extract-produce-discard) to a circular production model (extract-produce-reuse).

Due to the Grand Paris Express works planification, only one material was investigated in this paper. It comes from the Ile-de-France basin and is called Btram. It is an excavated limestone mud, coming from the construction of a tramway line in the Paris region in 2014, similar to materials that will be excavated during the Grand Paris Express (GPE) works.

From a geotechnical point of view, Btram granularity was from 80 μm - (47 wt-%) to 20-mm particles. Clay content (VBS) measurement following the NF P 94-068 standard gave a result of 0.5 g/100 g of analyzed material. According to the NF P 11-300 standard and the French GTR guidebook (MELT 2000), this material can

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be classified as “A1 soil.” It corresponds to a fine soil, composed of silts or clays whose consistency can easily change with small water content variations. In the case of a valorization of excavated material for road construction, it shows that Btram will probably need a hydraulic road binders (HRB) treatment in order to be stabilized and have sufficient mechanical properties.

Furthermore, the Btram valuation requires chemical, mineralogical, and environmental characterization to adapt HRB formulation and treatment. As excavated materials, tunnel boring muds are classified as wastes by French legislation. In the case of valorization in road construction, environmental specifications such as defined by the measures of French ministerial decree of December 12, 2014 (Arrêté 2014), and by the French methodological guide (SETRA 2011) have to be respected.

In the case of the Grand Paris Express project, some environmental problems were at stake and linked to the presence of sulfates and molybdenum (Mo). Their threshold crossing was identified by preliminary study and report from the environmental authority (Autorité environnementale 2018). With this observation, a particular focus on molybdenum was achieved in this study.

Molybdenum is present into Paris basin soils in low concentration, with contents from undetectable values to 1.5 ppm (Baize 2000; Darmendrail 2000; Gis Sol 2011a, b). Thus, it was necessary to characterize molybdenum and especially its speciation. Synchrotron analyses and leaching tests were performed to determine the oxidation state of molybdenum and its potential mobility.

Molybdenum is mainly found in nature as molybdenite (MoS_2), which is the most abundant molybdenum ore carrier (Smith et al. 2009; Breillat et al. 2014). It can also be found combined with other minerals like powellite ($\text{Ca}(\text{Mo},\text{W})\text{O}_4$), ferrimolybdite ($\text{Fe}_2(\text{MoO}_4)_3$), and wulfenite (PbMoO_4) (Jarrell et al. 1980; Barceloux 1999; Adriano 2001; Xu et al. 2013; Breillat 2015). The oxidation state of several minerals containing molybdenum is detailed in Table 1.

Due to the molybdenum content of the mud being low, it was difficult to identify and characterize it in soils. Thus, it

was necessary to concentrate this heavy metal through several processes, such as:

1. A *granular splitting*, considering that heavy metals are generally located in the fine fraction of materials.
2. A *thermal treatment*, which consists in a sample calcination of the mud at 950 °C, as it is mainly composed of calcareous material. This could allow to concentrate molybdenum by eliminating the CO_2 .

Such experiments were carried out on the material, but the molybdenum content obtained was too low to be characterized. Therefore, they are not detailed in this paper.

3. A *chemical treatment*, which is mostly mentioned in the literature as sequential extraction. Developed by Tessier et al. (Tessier et al. 1979), it allows to identify trace elements according to the mineralogical phase they are coming from. It consists in successive uses of reagents with increasing aggressiveness, leading to the solubilization/dissolution of specific compounds (carbonates, oxy-hydroxide, organic matter, etc.). Other extraction methods exist like the procedure established by the Community Bureau of Reference (BCR) of the European community commission (Ure 1991) and revisited by Rauret et al. (Rauret et al. 1999). Sequential extraction procedure by Alvarez et al. (Alvarez et al. 2005) can also be mentioned.

As the studied material was a limestone mud, the aforementioned protocols could be unadapted. Thus, a new protocol extraction was needed to completely dissolve calcite in the sample. A specific acid nitric extraction was developed at a laboratory scale. Following this process, it has been possible to verify whether trace elements (and especially molybdenum) are present in this limestone phase or not (Reddy and Gloss 1993).

The studied mud (Btram) environmental impact is exposed in this paper with a focus on sulfates and molybdenum. The speciation of molybdenum was studied after the development of a specific chemical extraction protocol for such a soil.

Methods

Chemical and mineralogical characterizations

Several analytical techniques have been carried out in order to clearly identify chemical and mineralogical elements constituting the Btram raw mud sample.

Chemical composition was determined by X-ray fluorescence analysis (Bruker S4 Pioneer) on the Btram sample which was previously oven dried at 105 °C, grounded ($\varnothing < 80 \mu\text{m}$), and compacted to obtain pellets.

Table 1 Listing of the main minerals containing molybdenum and their oxidation states (Breillat 2015)

Minerals	Chemical formula	Oxidation state
Molybdenite	MoS_2	IV
Molybdite	$\text{MoO}_3, \text{H}_2\text{O}$	VI
Wulfenite	$\text{Pb}(\text{MoO}_4)$	VI
Ferrimolybdite	$\text{Fe}_2(\text{MoO}_4)_3 \cdot 8(\text{H}_2\text{O})$	VI
Powellite	$\text{Ca}(\text{MoO}_4)$	VI

In order to identify and quantify traces of heavy metals in the material, at first step, acid and microwave digestion was carried out on the raw mud sample. Then ICP-AES analyses on eluate were performed (Agilent ICP-AES 5110 System).

Mineralogical phases were identified using an X-ray diffractometer (XRD). The device was a Bruker D8 Advance equipped with a cobalt anticathode, an anode voltage of 35 kV, and a current of 40 mA. The analysis was performed on the same type of sample as for X-ray fluorescence.

A thermogravimetric analyzer (TGA) was used to quantify calcite content in raw mud sample. The TGA was a NETZSCH STA 449 F3 Jupiter instrument equipped with an acquisition system recording mass variations during temperature increase, from room temperature to 1000 °C with a 3 °C/min step.

Scanning electron microscopy (SEM) was used to detect and characterize potential pollutants and especially molybdenum (Mo). The microscope was a Hitachi S-4300SE/N, coupled with an energy dispersive X-ray spectrometer (Thermo Scientific Ultra Dry EDS detector) for phases chemical analyses.

Regarding organic contaminants present in Btram sample, they were identified using several analysis techniques, as described below.

First, a determination of the organic matter content was done by the loss on ignition according to the XP P 94-047 standard. The sample was put into an oven for 3 h at 475 ± 25 °C. A second test was then performed but at 950 ± 25 °C for at least 1 h as required in the NF EN 1744-1 + A1 standard. It allowed to quantify carbon dioxide (CO₂) content and volatile oxidizable elements present in the sample.

Following the same standard (NF EN 1744-1 + A1), the potential presence of humus and fulvo acid was determined. According to this standard, if humus detection is positive, a determination of fulvo acid is required.

Environmental tests

Different analyses on Btram raw mud were performed to determine environmental behavior.

Leaching tests at natural pH following the NF EN 12457-2 standard (batch tests) were first carried out on the raw mud to study the mobility of contaminants such as heavy metals and anions. The sample was put into a normalized volume of distilled water and was stirred during 24 h. The liquid volume to solid mass ratio (L/S) was equal to 10. The solubilized heavy metals were quantified by ICP-AES analysis on eluate and the solubilized anions by a Dionex ICS 3000 ion chromatography.

In addition, specific analyses concerning organic contaminants were performed. They were determined on the raw mud by several analytical techniques, such as total organic carbon (TOC) content after dry combustion (following the NF ISO 10694 standard), hydrocarbon indices C10-C40 (according to the NF EN ISO 16703 standard), volatile aromatic and halogenated hydrocarbons (CAV-BTEX) (following the NF EN ISO 22155 standard), polycyclic aromatic hydrocarbons (PAH) content (according to the NF ISO 18287 standard), and organochlorine pesticides and polychlorinated biphenyls (PCB) content (following the NF ISO 10382 standard).

It was also necessary to study the pH impact on leaching test in order to determine the contaminant mobility under certain

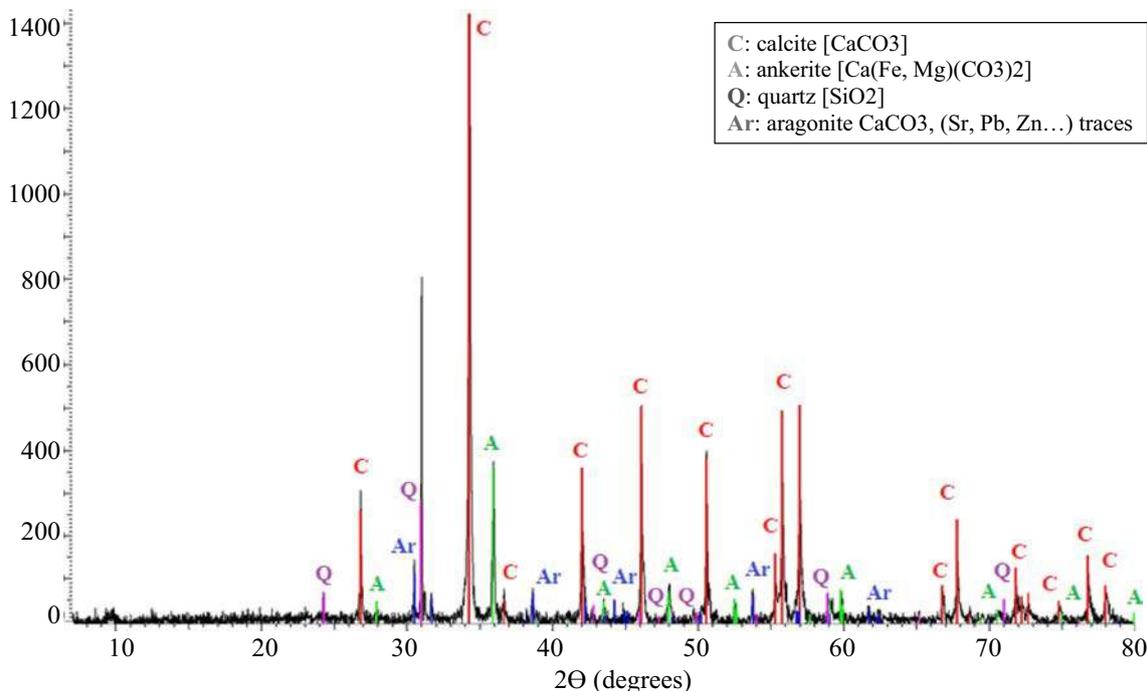


Fig. 1 Btram mineralogical composition obtained by X-ray diffraction analysis

Table 2 X-ray fluorescence analysis on Btram

Btram	
Elements	Concentrations (wt-%)
C*	10.2
O	50.0
F	0.2
Na	0.1
Mg	2.4
Al	0.7
Si	3.2
S	0.2
Cl	Traces
K	0.2
Ca	32.0
Ti	Traces
Mn	Traces
Fe	0.7
Sr	0.1
* TGA value	< 0.1% = Traces

specific conditions (e.g., high-pH conditions in the case of treatment with hydraulic binders). Some tests were performed following the NF EN 14429 standard. It consists of a 48-h leaching test in batch, with a L/S ratio = 10. The leachant was composed of more or less acid or base predetermined content, in order to reach and stabilize the required pH value and quantify its impact on heavy metals and anions mobility. The same analytical system was used for eluate analyses, as it was previously described.

Focus on the molybdenum characterization

Molybdenum concentration protocol

The purpose of chemical extraction was to concentrate the molybdenum to facilitate its analysis. Several extraction methods were experimented such as the protocol developed

Fig. 2 Btram thermogravimetric analysis

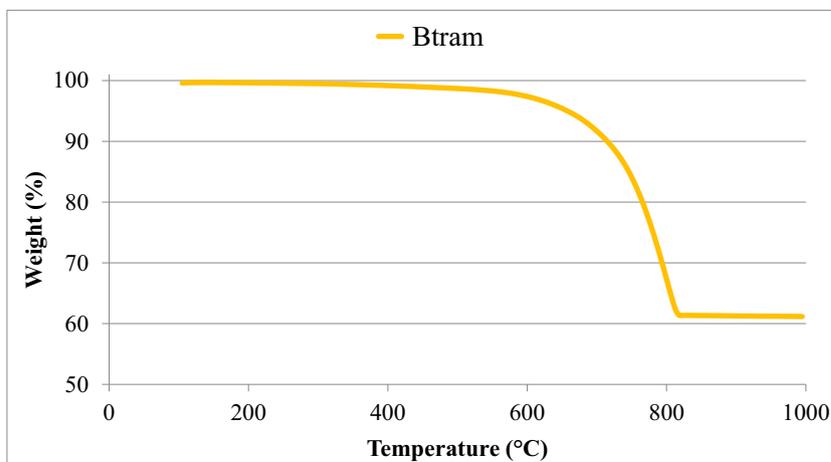
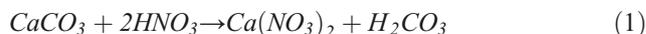


Table 3 Elements content on dry mater Btram

Contaminants	Methods	Unit	Contaminants content on dry matter
Arsenic (As)	Acid and microwaves digestion	ppm	5.9
Barium (Ba)			108
Cadmium (Cd)			1.0
Chrome (Cr)			18.5
Copper (Cu)			2.9
Mercury (Hg)			< 3.7
Molybdenum (Mo)			3.2
Nickel (Ni)			3.7
Lead (Pb)			4.7
Antimony (Sb)			< 7.7
Selenium (Se)			< 9
Zinc (Zn)			62.8

by Tessier et al. (Tessier et al. 1979), the BCR protocol revisited by Rauret et al. (Rauret et al. 1999), and the protocol by Alvarez et al. (Alvarez et al. 2005). However, since the main and targeted fraction of Btram is limestone, only the first extractions steps focusing on carbonates were carried out for all the protocols described above.

The previous protocols were not necessarily suitable for soil with high calcareous content; a new protocol based on nitric acid extraction was developed with the aim to dissolve all the Btram carbonated fraction. For this purpose, the concentration of H^+ ion required for the complete dissolution of the calcite ($CaCO_3$) was calculated in order to formulate a reagent according to the following equation:



To prevent an overly aggressive extraction with the other phase of the material, the L/S ratio was set at 200 with a nitric acid concentration of 0.1 mol/L in a volume of distilled water. After 3 h of agitation, the solution that decanted for 15 min was filtered through a 0.45- μ m Whatman filter. The leachate

Table 4 Organic contaminants contained into Btram

Analysis	Methods	Unit	Btram
Organic matter content at 450 °C	XP P 94-047	wt-%	2
Loss on ignition at 950 °C	NF EN 1744-1 + A1	wt-%	38.11
Humic mater	NF EN 1744-1 + A1	-	Negative
Fulvic acid	NF EN 1744-1 + A1	-	-

was analyzed by ICP-AES to quantify leached elements. The concentrated solid phase was collected and oven dried at 40 °C, and then acid and microwave digestion was carried out. Finally ICP-AES analyses were performed to quantify elements into concentrated solid phase.

Characterization of molybdenum speciation

Analysis by X-ray absorption spectroscopy was performed to determine molybdenum speciation.

X-ray absorption near-edge structure (XANES) spectrum at the molybdenum *K*-edge (20 keV) was collected on SAMBA beamline and SOLEIL synchrotron, located in Gif-sur-Yvette. The SAMBA beamline was equipped with a Si (220) monochromator and a Si Drift (SDD) 4 elements detector.

Two types of analyses were carried out. First, the monochromator was placed at an energy above the molybdenum *K*-edge, i.e., at 21 keV. At this energy, molybdenum emitted fluorescence, as well as all elements present in the sample with electronic transitions at lower energies. Then a “multi-channel analyzer” spectrum (“MCA” spectrum) was recorded by the SDD fluorescence detector for 60 s, allowing qualitative analysis (the energy position of fluorescence peaks in the MCA spectrum being specific to the element) and semiquantitative analysis (relative proportion of peaks). The window materials and environment precluded the detection of elements lighter than Ca. The second analysis consisted in collecting the Mo *K*-edge XANES spectrum of the sample and comparing it to the spectra of “reference” samples or from literature. It allowed to determine the oxidation state of molybdenum.

Table 5 Organic contaminants contained into Btram sample

Contaminants	Methods	Btram	Maximal values specified in the French ministerial order of December 12, 2014
TOC	NF ISO 10694	< 3700	30000
Hydrocarbon indices C10–C40	NF EN ISO 16703	41	500
CAV-BTEX	NF EN ISO 22 155	UD	6
PAH	NF ISO 18287	UD	50
PCB	NF ISO 10382	UD	1
UD: undetected			

Unit: ppm

Results and discussion

Chemical and mineralogical identification

In view of the results of DRX, X-ray fluorescence (XRF), and TGA analyses, Btram was proved to be mainly limestone mud. Mineralogical composition, obtained by XRD exposed in Fig. 1, showed that Btram was mainly composed of calcite, ankerite, aragonite, and quartz. Chemical composition, obtained by XRF given in Table 2, showed that calcium was the main detected element (32 wt-%), reflecting a matrix essentially composed of calcite as carbon was also detected (10.2 wt-%). Silicon and magnesium were detected in a few wt-% (respectively, 3.2 and 2.4 wt-%). Other elements were identified but their content was less than 1 wt-% or as traces. Furthermore, thermogravimetric analysis (TGA), as shown in Fig. 2, allowed to quantify calcite content by measuring the loss on ignition value between 600 and 850 °C, corresponding to the calcite decarbonation. Btram was composed of 84 wt-% calcite.

Acid and microwave digestion was carried out to determine the heavy metals content in Btram. The obtained results, exposed in Table 3, showed that the molybdenum content was 3.2 ppm. It was higher than the INDIQUASOL values which established a maximal content of 1.5 ppm for the Ile-de-France region. But from an analytical point of view, this value was very weak and SEM-EDS analyses did not allow to detect molybdenum in the studied sample.

Organic contaminants contained in Btram sample are listed in Table 4. The organic matter content was low with 2 wt-% obtained by the loss on ignition at 475 °C. The obtained loss on ignition at 950 °C was 38.11 wt-%. This result coincides

Table 6 Leachate analyses after leaching test (24 h in batch)

Contaminants	Methods	Btram	Maximal values specified in the French ministerial order of December 12, 2014
Arsenic (As)	NF EN ISO 17294-2	< 0.03	0.5
Barium (Ba)		< 0.7	20
Cadmium (Cd)		< 0.015	0.04
Chrome (Cr)		< 0.05	0.5
Copper (Cu)		< 0.05	2
Mercury (Hg)		< 0.001	0.01
Molybdenum (Mo)		0.46	0.5
Nickel (Ni)		< 0.1	0.4
Lead (Pb)		< 0.1	0.5
Antimony (Sb)		< 0.05	0.06
Selenium (Se)		< 0.1	0.1
Zinc (Zn)		< 0.5	4
Chlorides (Cl)	NF EN ISO 10304-1	< 100	800
Sulfates (SO ₄)		1500	1000
Fluorides (F)		< 10	10
Soluble fraction	Calculations based on dry residues	2500	4000
TOC	NF EN 1484	53	500
Phenol indices	NF EN ISO 14402	< 0.1	1
pH	NF EN ISO 10523 (A)	8,6	-

Unit: ppm

with calcite content estimated with TGA analysis (Fig. 2). Humic matter was undetected into the studied sample. According to the NF EN 1744-1 + A1 standard, fulvic acid was considered as being absent in a material when humic matter was undetected.

Environmental behavior

Regarding organic pollutants, the contents complied with the French regulation as detailed in Table 5. The leaching test results following the NF EN 12457-2 standard (24 h in batch) given in Table 6 showed that only sulfates (1500 ppm) were exceeding the inert threshold value (1000 ppm) specified in the French ministerial order of December 12, 2014 (French regulation). These sulfates exceedance were previously mentioned by the environmental authority (Autorité environnementale 2018) and were also found on tunnel boring mud from other projects such as for the Lyon-Turin line (Colas 2012; Chaussadent et al. 2013). In contrast, the leachate molybdenum value did not exceed the limit value as expected from preliminary study, but it was very close with 0.46 ppm for a specification of 0.5 ppm. However, it implies that molybdenum could be a problematic heavy metal from an environmental point of view. Thus, it was necessary to study its mobility under different conditions and to characterize it as finely as possible.

The mobility of heavy metals contained in Btram can be studied by comparing the leachate values with the chemical composition obtained by acid and microwave digestion. For example, barium (Ba) content was quite high with 108 ppm (Table 3), but the leachate value was very weak (less than 1 ppm (Table 6)), reflecting the low mobility of this heavy metal. The same phenomenon occurred for molybdenum with a 3.2 ppm total content and a leachate value of 0.46 ppm.

In order to study the heavy metals mobility contained in Btram under different pH conditions, a leaching test following the NF EN 14429 standard was performed. As shown in Table 7, the first noticeable result was that without acid or base addition (listed “N” in the table with a pH value of 9.1), molybdenum leaching (0.51 ppm) slightly exceeded the French specification (0.50 ppm) whereas that was not the case after the first leaching test performed (Table 6). This can be explained by the fact that this “different pH leaching test” duration was 48 h (24 h for the first test), allowing more time for the molybdenum to be solubilized. Results showed that molybdenum leaching remained globally around 0.51 ppm in basic condition. The values decreased in acid pH conditions, from 0.51 ppm to 0.4 ppm to a pH value of 6.5 and even to 0.19 ppm for a pH value of 4.9. This phenomenon was mentioned in the literature where molybdenum mobility decreased at low pH value especially with a Mo adsorption peak for both ferric and aluminum oxides in the range of pH 4 to 5 or in clay minerals near pH 3 (Goldberg et al. 1996; Das et al. 2007; Xu et al. 2013).

Table 7 pH influence on Btram heavy metals leaching

Elements	Contents in raw Btram	NF EN 12457-2	pH											Inert
			4.9	6.5	7.0	7.5	N	10.0	11.1	12.0	13.0	13.2		
As	5.9	< 0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.9	1.2	0.5
Ba	108	< 0.7	45	6.7	3.4	2.2	1.6	1.4	0.6	0.4	0.7	2.9	20	
Cd	1	< 0.015	< 0.02	< 0.04	< 0.04	< 0.04	< 0.02	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	0.04	
Cr	19	< 0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.2	0.5
Cu	2.9	< 0.05	< 0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2	0.3	2
Mo	3.2	0.46	0.19	0.40	0.45	0.47	0.51	0.504	0.51	0.501	0.63	0.53	0.5	
Ni	3.7	< 0.1	0.41	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.4
Pb	4.7	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2	0.5
Sb	<7.7	< 0.05	0.097	< 0.06	< 0.06	< 0.06	< 0.2	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	0.06
Se	<9	< 0.1	0.17	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	0.16	0.37	0.64	0.52	0.1	
Zn	63	< 0.5	1.72	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.19	1.29	4	

“inert”: threshold specified in the French ministerial order of December 12, 2014

Unit: ppm

Other heavy metals showed a specific behavior in accordance with pH conditions. Thus, when the leachate pH was around 5 (acid conditions), there were a threshold crossing for barium, nickel, antimony, and selenium. In basic conditions, selenium was in excess like arsenic.

N.B.: for analytical reasons, it was impossible to quantify anions under acid conditions

Regarding anions analyzed by ion chromatography in basic pH conditions and presented in Table 8, their behaviors were different. Sulfates content always exceeded the threshold and the leachate values increased with increasing pH value. For fluorides, there was also an increase of leachate value with threshold crossing at pH values from 11. Chlorides remained under the threshold.

Taking into account these results, and especially the leaching increase of anions and some heavy metals under basic pH conditions, it will be important to study the environmental behavior of Btram, especially when treated with hydraulic road binders (HRB) which leads to an increase of pH value.

Molybdenum concentration by chemical extraction

A chemical way was experimented to concentrate molybdenum in the studied material with different extraction protocols such as: (Tessier et al. 1979), the revisited BCR protocol by (Rauret

et al. 1999) and the (Alvarez et al. 2005). In our case, only the first steps of sequential extractions were done in order to attack carbonates and avoid the dissolution of other phases in Btram.

As shown in Fig. 3, these three extraction protocols were not effective due to too large amount of carbonates in Btram. The molybdenum concentration remained around 3 ppm for the first two protocols and a marginal improvement obtained with the Alvarez protocol with 4.1-ppm molybdenum.

In order to solve concentration issues previously encountered, it was decided to apply a new method described in the “Molybdenum concentration protocol” section: nitric acid extraction with the aim to dissolve all the carbonated fraction in Btram. As shown TGA results in Fig. 4, the extraction protocol was successful with the complete carbonates dissolution. Carbonates dissolution is observed by the disappearance of the loss ignition between 600 °C and 850 °C, characteristic of calcite decarbonation in the raw sample. Furthermore, this decarbonation was also observed at the sample scale with a mass decrease: from 5 g before extraction, only 0.8 g was collected after filtration, corresponding to the dissolution of 84 wt-% of calcite.

Heavy metals concentration was determined on the solid residue after nitric acid extraction. Results were compared with those obtained on raw material. As shown in Table 9, the solid residue after nitric acid extraction concentrated heavy

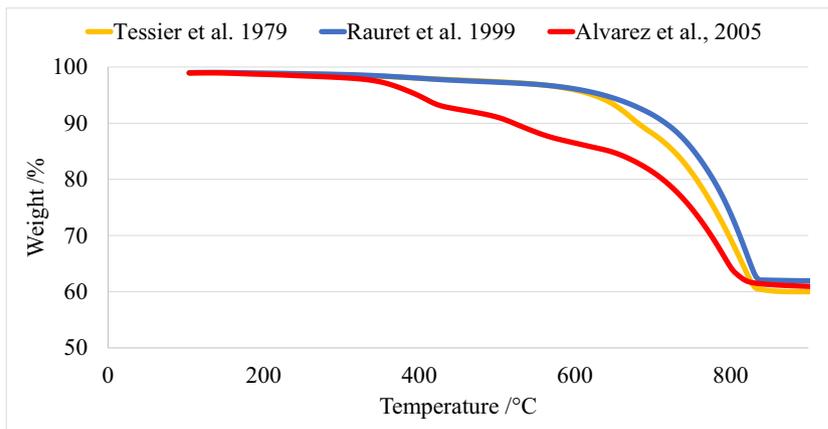
Table 8 pH influence on Btram anions

pH	7.5	N	10.0	11.1	12.0	13.0	13.2	Inert
Fluorides	5	7	7.3	13.6	15.3	< 50	< 100	10
Chlorides	25	21.5	20.0	33.8	20.9	21.0	21.1	800
Sulfates	1550	1595	1660	1660	1680	1760	2210	1000

“inert”: threshold specified in the French Ministerial Order of December 12, 2014

Unit: ppm

Fig. 3 TGA comparison of different extraction protocols



metals, especially molybdenum content increasing from 3.2 to 21 ppm. It implied a concentration of about 6 times higher.

In order to ensure that heavy metals and molybdenum had not been leached with nitric acid, ICP-AES

analysis was carried out on it. Elements balance before and after the extraction was done (last column in Table 9).

For example, the equation 2 showed the case of arsenic:

$$\begin{aligned}
 &84 \text{ wt-}\% * 2.0 \text{ ppm leachate in reagent} + 16 \text{ wt-}\% * 27 \text{ ppm of residual content} = 6.0 \text{ ppm of total content} \\
 &\text{With } 84 \text{ wt-}\% \text{ corresponding of the calcite content on raw Btram which dissolved by acid leaching} \\
 &\text{And } 16 \text{ wt-}\% \text{ the other mineral phases after extraction.}
 \end{aligned} \tag{2}$$

These 6.0 ppm obtained for arsenic have to be compared with the initial raw material content which was 5.9 ppm. It showed that values matched and it means that this heavy metal balance before and after extraction allowed to evaluate the element distribution between the nitric acid solution and the solid residue after the extraction.

It was interesting to apply this calculation for molybdenum. But, due to too high detection limit, the leaching value after nitric acid extraction was not precisely measured (< 1.2 ppm). Without taking into account this value, the Eq. 3 gave the following result:

$$\begin{aligned}
 &16 \text{ wt-}\% * 21 \text{ ppm of residual content} \\
 &= 3.3 \text{ ppm of total content}
 \end{aligned} \tag{3}$$

These 3.3 ppm in the solid residue were very close to the 3.2 ppm detected into the raw material. It means that all molybdenum was contained in the solid residue obtained after extraction, and therefore, it was not bounded with carbonates. It was confirmed by the absence of molybdenum in acid leaching solution. The result was in accordance with other studies (Reddy and Gloss 1993; Adriano 2001) which show that carbonate phases were not a significant sorbent for Mo in soils.

Generally, the heavy metals balance before and after extraction was reliable, but there were some exceptions like cadmium (Cd) and lead (Pb) where a difference with the raw material content was noticed, probably due to analytical issues.

Fig. 4 TGA analyses on Btram before and after calcite dissolution, thanks to the nitric acid extraction protocol

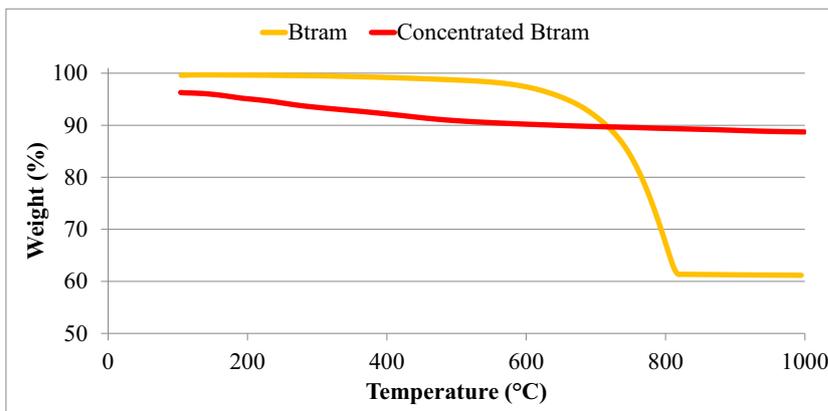


Table 9 Contaminants comparison between raw and concentrated Btram after chemical extraction—total content and leaching values

Contaminants	Total content in the raw material	Leaching value for the raw material (NF EN 12457-2)	Leaching value after nitric acid extraction	Total content in the solid residue after nitric acid extraction	Heavy metals balance before and after extraction
As	5.9	< 0.03	2.0	27	6.0
Ba	108	< 0.7	88	222	109
Cd	1	< 0.015	2.6	< 0.2	2.2
Cr	19	< 0.05	3.9	120	22
Cu	2.9	< 0.05	3.1	12	5
Hg	< 3.7	< 0.001	-	< 1.2	-
Mo	3.2	0.46	< 1.2	21	3.3
Ni	3.7	< 0.1	2.3	23	5.6
Pb	4.7	< 0.1	7.7	12	8.3
Sb	< 7.7	< 0.05	< 1.1	7.5	1.2
Se	< 9	< 0.1	< 0.8	2.6	0.4
Zn	63	< 0.5	33	106	45

Unit: ppm

Molybdenum speciation

As XRD and SEM-EDS analyses were not sufficient to identify and characterize molybdenum, synchrotron analyses were performed on a concentrated Btram sample after nitric acid extraction (solid residue). Obtained results are exposed in Figs. 5 and 6.

First, MCA (multi-channel analyzer) spectrum obtained on the raw material (Fig. 5a) revealed the presence of several elements, including a significant concentration of strontium (Sr). The sample also contained iron (Fe) and copper (Cu). The peak corresponding to the K alpha emission of molybdenum was, as expected, very weak.

In addition, about 40 XANES spectra were measured on raw Btram, localized at the molybdenum K-edge and then

averaged. It is exposed in Fig. 5b with normalized XANES spectra of Mo(IV) and Mo(VI), collected at the SAMBA line from another research work (Havelius et al. 2011). A previous study (Ressler et al. 2002) demonstrated that molybdenum oxidation degree could be determined from the second oscillation observed at the maximum absorption of the XANES spectrum at molybdenum K-edge. This oscillation differed by about 9.3 eV between Mo(IV) (20035.7 eV) and Mo(VI) (20045 eV) according to this study. The second oscillation from concentrated Btram spectrum was about 20038.6 eV. Compared with Mo(IV) and Mo(VI) standards spectra, it gave a distribution for concentrated Btram sample of approximately 70% of Mo(IV) and 30% of Mo(VI).

The phase which could contain the 70 % of Mo(IV) was probably molybdenite (MoS_2) in Btram. According to the

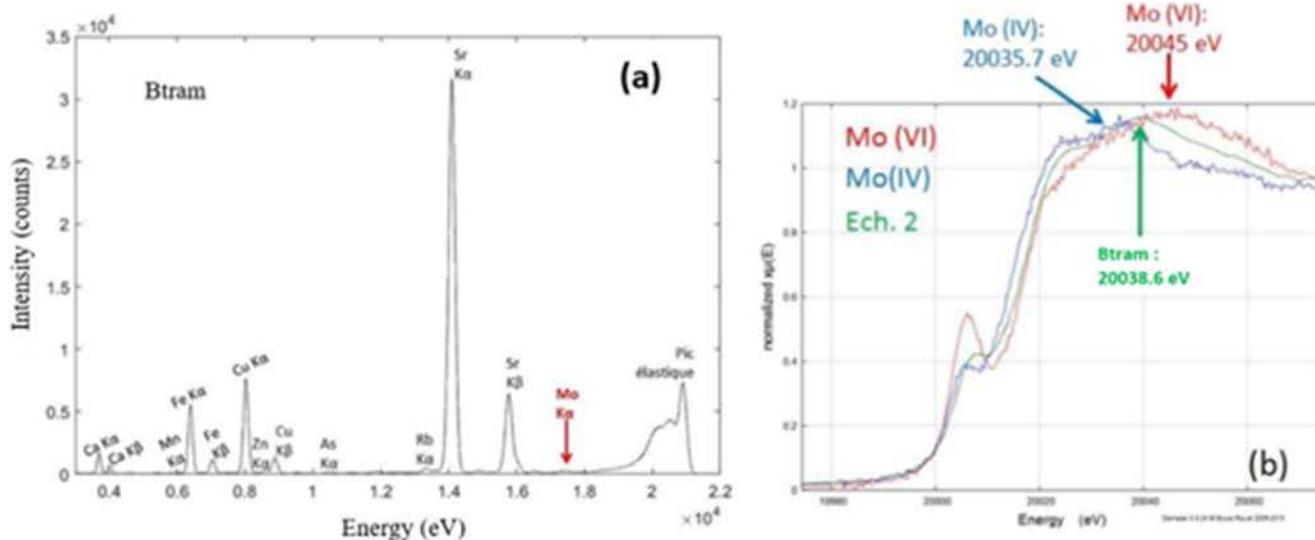


Fig. 5 MCA and XANES spectra for Btram

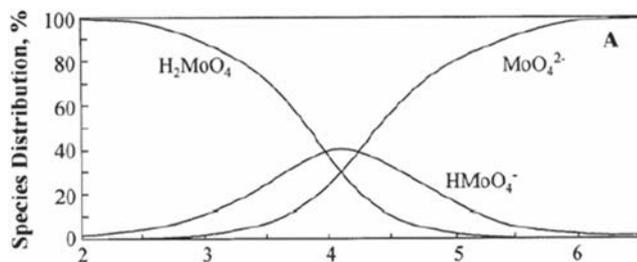


Fig. 6 Molybdenum speciation in function of pH (Adriano 2001)

literature, this phase was the principal source of molybdenum in soils (Adriano 2001) and with an oxidation state of (IV) (Breillat 2015). Moreover, molybdenum was mainly found at this oxidation state under anoxic conditions (Brookins 1989). So, this molybdenum sulfide was probably formed by the past when the Paris basin was submerged and when molybdenum was under anoxic conditions in a gypsum environment by molybdate reduction following (Amrhein et al. 1993) this equation:



However, concerning the 30% of Mo(VI), it was more difficult to determine into which mineral phases could be contained. Under oxic and suboxic conditions, with a pH value comprised between 4 and 8, Mo(VI) was in the most stable state in solution and was mainly represented in nature in the anionic form of molybdate MoO_4^{2-} (Xu et al. 2013; Kendall et al. 2017) and also other phases depending on pH and Eh. For instance, molybdenum species in solution when pH value was under 4.2 were “molybdic acids” such as HMoO_4^- and H_2MoO_4 , as it can be seen in the Fig. 6. As Btram pH value was above 6, MoO_4^{2-} should be the predominant ion, and for alkaline soil solution, the dissolved Mo species could be dominated by CaMoO_4 and MgMoO_4 (Reddy and Gloss 1993).

But, Adriano (2001) gave some ions such as Na, K, Mg, and Ca, where the molybdate did not form strong complexes, so the hypothesis that Btram molybdenum was not bounded with one of those elements could be established. In another hand, the sorption of molybdate was very strong with ferric and aluminum oxides such as goethite, gibbsite, and clay minerals (Goldberg et al. 1996; Adriano 2001) with a maximum adsorption at low pH values (between 4 and 5) and another small adsorption at a pH value of above 8 for Fe and Al oxides (Xu et al. 2013). As a consequence, the 30% of Mo(VI) could be bounded to these minerals, but it has to be confirmed by analyses.

Conclusions

To upgrade GPE muds, their impact on environment must be assessed. Hence, an analysis of samples and a search for their

pollutants has to be carried out. The conclusions for the limestone mud called Btram were as follows:

1. Only the sulfates content presented inert threshold crossing from the French ministerial order (December 12, 2014) with the application NF EN 12457-2 standard. Molybdenum content was close to inert threshold hence a focus on this element which could be problematic.
2. The content of sulfates, molybdenum but also selenium, arsenic, and fluorides increased with basic pH conditions which could be obtained with treatment with hydraulic road binders (HRB) used to improve geotechnical performances of the mud studied.
3. To study molybdenum speciation, a concentration of it was necessary. The new protocol based on nitric acid extraction was successful with the complete carbonates dissolution for limestone mud (84% carbonate in Btram). It led to a molybdenum concentration 6 times higher than in the raw material and allowed to show that molybdenum is not bounded to carbonate phase.
4. Concerning the molybdenum speciation study, MEB-EDS and XRD analyses were not sufficient to determine it. Only synchrotron analyses, and especially XANES spectra, allowed to obtain more information and gave the oxidation state of molybdenum in the studied sample. The result showed that molybdenum was distributed as following: 70% of Mo(IV) (probably as molybdenite) and 30% of Mo(VI).

To comply with the environmental criteria of the regulations, the mud must be treated with a hydraulic binder in order to reduce the mobility of pollutants in addition to achieving the necessary mechanical performance linked to the geotechnical characteristics. This is the objective of continuing this study.

Acknowledgments The authors would like to thank EIFFAGE Infrastructures company for its support and the synchrotron beamline staff of Soleil at Gif-sur-Yvette for their valuable contribution to this work.

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