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# **Incorporation of antimony-bearing mining wastes into clinker Portland raw feed: the difficulty of Sb analysis in calcium silicates**

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## **Abstract**

Within the global trend to valorize various mineral wastes as substituents in Portland cement clinker raw feed, mining wastes are promising candidates. However, they might still contain high levels of metallic elements. Their fate in the kiln is not always understood as well as their incorporation within the various clinker's phases. This is especially the case for antimony. Its in-situ microanalysis by the means of energy-dispersive spectroscopy is tricky since several of its L-lines ( $L_{\alpha 1}=3604,72$  eV,  $L_{\alpha 2}=3595,32$  eV) overlap with calcium lines ( $K_{\alpha 1}=3691,68$  eV,  $K_{\alpha 2}=3688,09$  eV). Hence, at low concentrations, it is not possible to visualize its characteristics peaks. Increasing the counting rate by increasing the acceleration current results in the generation of spurious sum peaks, rendering the analysis not viable. Wavelength dispersive spectroscopy

(i.e. electron microprobe) allows a better spectral resolution and quantification of Sb in the clinker phases. In a Portland cement clinker doped with 1 % of Sb-bearing mining waste, the  $\text{Sb}_2\text{O}_3$  content in belite and alite is in the 0.2-0.4 wt.% range as well as for  $\text{C}_3\text{A}$ ; in  $\text{C}_4\text{AF}$  the content is higher, from 1.4 wt.% to 2 wt.%. However, there are microstructural evidences that Sb forms blebs from less than 1 micrometer in diameter up to 10 micrometers, included in calcium silicates. Hence, its incorporation in the lattice of calcium silicates is dubious. However, for ferrites and aluminates there is no microstructural evidence for remaining Sb-bearing phases, suggesting a direct incorporation in crystal lattices.

**Keywords:** Mining wastes; antimony; clinker; microanalysis

## **1 MATERIALS AND METHODS**

### **Mining wastes**

Mining waste are defined as “waste products originating, accumulating and present at mine sites, which are unwanted and have no current economic value”<sup>1</sup>. Each mining step is likely to generate mining waste, which covers a wide range of geochemical, mineralogical and physical properties<sup>2,3</sup>. Similarly, their chemistry is determined by the ore type and the manufacturing procedure. France has a long history of mining and the extraction residues pose multiple ecological hazards.

The cement industry, for example, which requires a large amount of raw materials, is a good candidate for the incorporation of various wastes in its raw feed. Its implications are multiple; cement production records up to 7 percent of global anthropogenic greenhouse gas emissions, in

fact, it is a significant source of CO<sub>2</sub> emissions<sup>4</sup>. The main part of the emission occurs during the clinkerization process in the cement kiln<sup>5</sup>.

Hence, in order to minimize the natural resource exploitation by recycling mineral residues, their integration into cement raw materials is an interesting method of re-use<sup>6,7</sup> in order to favor circular economy to avoid the piling up of wastes in the environment. Hence, it replaces a portion of the cement's raw resources, which are non-renewable natural materials, mainly clays and limestones.

The mineral industry, and particularly the mining industry, is a typical example of a producer of recoverable mineral residues. For instance, the French Massif Central produced 50 000 tons of antimony, mostly from the Brioude-Massiac district. With all these quantities generated, it is obvious that tons of waste have been generated by these extractions, as such significant quantities of antimony waste can thus be a source of alternative materials ready to be recycled.

Antimony is known as a critical, mysterious and very volatile element; moreover, it is found in nature particularly associated with other elements such as sulfur and oxygen and not in its native form<sup>8</sup>.

Mine wastes s.s. results from mining operations of removing the overburden and host rocks of the ore body<sup>9</sup>. Tailings are processing wastes resulting from the treatment of the ore and will not be considered here. However, in order to give an idea of the amount of wastes which are likely to be produced during mining operations, one extracted ton of a 4.3% grade Sb ore<sup>10</sup> will produce 95.7% of waste, and this concerns only the ore body, not the extracted overburden.

Considering mine wastes from metallic mines, especially in old mining areas, they are still likely to contain various metallic elements worth exploiting<sup>11,12</sup>. Indeed, old mining methods were

likely to be less effective and cut-off grades were probably higher when resources were less critical than today.

The mine wastes investigated in this study are remains from antimony mines B and C in the French Massif Central. Although they cover important surfaces and constitute voluminous piles (Figure 1), they are in remote places and their overall volume is very small compared to active mines areas. Such small dumps are known to be problematic<sup>13</sup>. Hence, they are unlikely to form valuable mineral resources, but might be interesting as secondary material for raw feed. The present article focuses firstly on the characterization of these mine residues and secondly on the clinkers that are manufactured after firing an industrial raw material which it partially replaces.



*Figure 1. Mining wastes from the B mine, French Massif Central. **Note to the publisher: one column width***

### **The fate of heavy elements in Portland cement clinker**

This topic has been widely studied, and is still under investigation, since the incorporation of various mineral wastes in the clinker raw feed is a way of valorization<sup>14</sup>. All Portland clinker

phases are likely to incorporate foreign elements in their crystal structures. In some cases this incorporation can be done purposely, such as for example in the case of the stabilization of the high temperature  $\alpha$ -C<sub>2</sub>S polymorph by MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, BaO, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> or Cr<sub>2</sub>O<sub>3</sub><sup>15</sup>.

However, contrarily to previous studies dealing with the mixing of pure chemicals in the clinker synthesis (NiO, SnO<sub>2</sub>, ZnO<sup>16,17</sup>, CuO<sup>18</sup>...), the present work documents the incorporation of actual mining wastes, even more specifically wastes from former antimony mines. The challenge of working with mining waste lies in their varied mineralogy<sup>3</sup>, making their incorporation in a laboratory raw feed far more complex than working with pure chemical compounds. It must be noted that the incorporation of a stibnite-bearing ore in a raw feed, in order to study its mineralizing effect, has shown that it increases the burnability<sup>7</sup>.

In the case of wastes from Sb mines, within a gangue made generally of quartz – which will account for their richness in SiO<sub>2</sub>, many mineral species are likely to be present<sup>19</sup>:

- Sulfides: **stibnite** Sb<sub>2</sub>S<sub>3</sub>, pyrite FeS<sub>2</sub>...
- Oxydes: valentinite/sénarmontite Sb<sub>2</sub>O<sub>3</sub>, schafarzikite FeSb<sub>2</sub>O<sub>4</sub>, tripuhyite FeSbO<sub>4</sub>...
- Native elements: Sb, S,
- Silicates : chapmanite Fe<sub>2</sub>Sb(Si<sub>2</sub>O<sub>5</sub>)O<sub>3</sub>(OH)
- ...

This mineral diversity will account for very complex reactions during the clinkerization process. Although some studies covering a wide range of elements and their effect on cement quality had already been published<sup>20</sup> it concerns generally case-by-case studies. Mining wastes are generally polymetallic, rendering the range of possible interactions to a high amount.

Moreover, in the aforementioned list of minerals, they are likely to have different melting/volatilization temperatures as well as different behaviors in a high temperature kiln when intermixed with other materials.

Some contradictions can be emphasized in the scarce literature dealing with the incorporation of Sb-bearing wastes in the raw feed of Portland clinker. Indeed, while some authors argue for the formation of calcium antimonates <sup>20</sup>, some others have observed the incorporation of Sb within the interstitial phase <sup>21</sup>, but in any case it has been shown to be poorly volatile <sup>22</sup>.

### **The difficulty of antimony analysis by energy dispersive spectroscopy in clinker phases**

Despite its wide use in cement and concrete science, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) suffers from inherent limitations when it comes to analysis of elements in low concentrations <sup>23</sup>. In the specific case of elements with  $Z > 44$  (i.e. above Ru), the K lines are above 20 keV, hence the microscopist has to deal with many lower energy lines from the L (and sometimes M) family. In the specific case of Sb, the three main L lines ( $L_{a1}=3604,72$  eV,  $L_{a2}=3595,32$  eV,  $L_{b1}=3843,57$  eV; X-ray data booklet, Center for X-ray Optics and Advanced Light Source, Lawrence Berkeley National Laboratory) fall within the range of the Ca K lines ( $K_{a1}=3691,68$  eV,  $K_{a2}=3688,09$  eV). Hence, at low or trace concentrations, Sb is likely to not be detected because of those overlaps.

Thus, wavelength dispersive spectroscopy (WDS) appears as an interesting alternative to deal with such analytical sources of errors. While rarely applied to cementitious materials, its spectral resolution is better than EDS so dubious peaks in EDS are likely to be resolved by the means of WDS.

## **2 MATERIALS AND METHODS**

The mining waste samples were taken from former mining sites in the Massif Central, the mine B in the Haute-Loire department and the mine C from Puy-de-Dôme. The samples were dried and homogenized before their chemical and mineralogical properties were determined.

Portland clinkers were produced in the laboratory by combining the required amount of an industrial **clinker** raw feed with the replacement of the percentage of residues that allows the theoretical amount of phases, as given by the Bogue formulas, to be respected. The cement raw feed used in this study was supplied by Mineralab society.

After a five-minute mixing in an agate mill with agate balls, rotating at 180 rpm, the raw feed was pelletized, placed in an alumina crucible and heated to 1450 °C at a rate of 10 °C/min, held at this temperature for 45 minutes, and then cooled to 20 °C. The obtained clinkers were placed in a desiccator aiming to avoid any air reaction. Clinkers and wastes have been studied by X-Ray diffraction (Bruker D8 advance, Co anticathode) and scanning electron microscopy (Hitachi 4300 SE/N) coupled with energy dispersive X-ray spectroscopy (Ultradry, Thermo Scientific) before and after firing. Polished cross sections were produced by halving the sample, roughly grinding a flat surface, impregnating it in epoxy resin, then polishing using water-free lubricant (DP-Brown, Struers) and diamond pastes.

A Cameca SX100 electron probe microanalyser (EPMA) was used to perform quantitative elemental analysis. Quantifications were carried out at 15 kV, 15 nA. The acquisition time was set at 20s for each element. A LLiF crystal was used to detect the Fe and As  $K\alpha$  X-rays, a LPET crystal to detect the Ca, P, Ti  $K\alpha$  X-rays and Sb  $L\alpha$  X-ray and a TAP crystal to detect the Si, Al and Mg  $K\alpha$  X-rays. The standards used to quantify Si, Ca, Al, Fe, S, As, Sb, Ti and Mg were, respectively, wollastonite, **orthoclase**,  $Fe_2O_3$ , ZnS, GaAs, GaSb,  $MnTiO_3$  and MgO.



Peaks of Ca and Sb are located in the same spectral region, thus the locations to measure Ca and Sb backgrounds were carefully chosen. Ca and Sb background were respectively measured at -800 and +300.

### 3 RESULTS AND DISCUSSION

The results of the chemical analysis conducted on mining residues (Table 1) show the presence of high concentrations of antimony for the samples extracted from B and C mines (18.6 and 16.47 wt.%  $\text{Sb}_2\text{O}_3$  respectively).

Element	Unit	Clinker	Mine waste		Clinker with wastes	
			B	C	CP1B	CP1C
$\text{SiO}_2$	%	13,98	61,18	56,05	14,54	14,95
$\text{Al}_2\text{O}_3$	%	3,27	10,39	14,36	3,36	3,47
$\text{Fe}_2\text{O}_3$	%	1,68	1,86	2,43	1,69	1,70
CaO	%	43,58	0,06	0,04	43,41	42,99
MgO	%	0,68	0,33	0,66	0,68	0,68
MnO	%	0,05			0,05	0,05
$\text{K}_2\text{O}$	%	0,32	2,89	4,1	0,35	0,38
$\text{Na}_2\text{O}$	%	0,04	0,13	0,13	0,04	0,04
$\text{SO}_3$	%	0,1	2,25	3,5	0,12	0,16
$\text{TiO}_2$	%	0,17	0,17	0,67	0,17	0,18
$\text{Sb}_2\text{O}_3$	%		18,6	16,47	0,19	0,35
LOI	%	35,43			35,29	34,95
Total	%	99,41	97,86	98,41	100,00	100,00
Zn	$\text{mgkg}^{-1}$	-	582	-	5,80	N/A
Pb	$\text{mgkg}^{-1}$	-	1140	-	11,36	N/A
As	$\text{mgkg}^{-1}$	-	1830	3750	18,23	55,04
Zr	$\text{mgkg}^{-1}$	-	-	152	-	-
Rb	$\text{mgkg}^{-1}$	-	147	295	1,46	4,36
P	$\text{mgkg}^{-1}$	261	150	-	261,48	-
Cr	$\text{mgkg}^{-1}$	-	-	217	N/A	2,14
Sc	$\text{mgkg}^{-1}$	-	-	1260	N/A	12,43

*Table 1. Chemical composition of the reference clinker, antimony mine wastes from mines B & C and calculation of the clinker made with the addition of 1 % of wastes. – indicates that the elements were below the detection limit, N/A that the calculation is not applicable.*

Moreover, these samples are rich in SiO<sub>2</sub> (56-61%) but almost devoid of CaO (less than 1%). The presence of As in those wastes (1830 and 3750 mg/kg for B and C wastes, respectively) also encourages the necessity to remove them from the environment.

The phase identification by XRD (Figure 2) reveals that those wastes are very similar to each other, the differences lying in their respective modal mineral abundance. Quartz is predominant in both wastes. In the C mine wastes, muscovite is abundant whereas it is almost absent in wastes from the B mine wastes. Orthoclase is present in a minor amount, but its main peaks overlap with quartz. A minor amount of rutile is present. Regarding Sb-bearing phases, stibnite (Sb<sub>2</sub>S<sub>3</sub>) and valentinite (Sb<sub>2</sub>O<sub>3</sub>) can be identified. Finally, a FeSb<sub>2</sub>O<sub>4</sub> phase<sup>24</sup>, structurally identical to the mineral schafarzikite, is abundant in wastes from the C mine but almost absent from mine B.

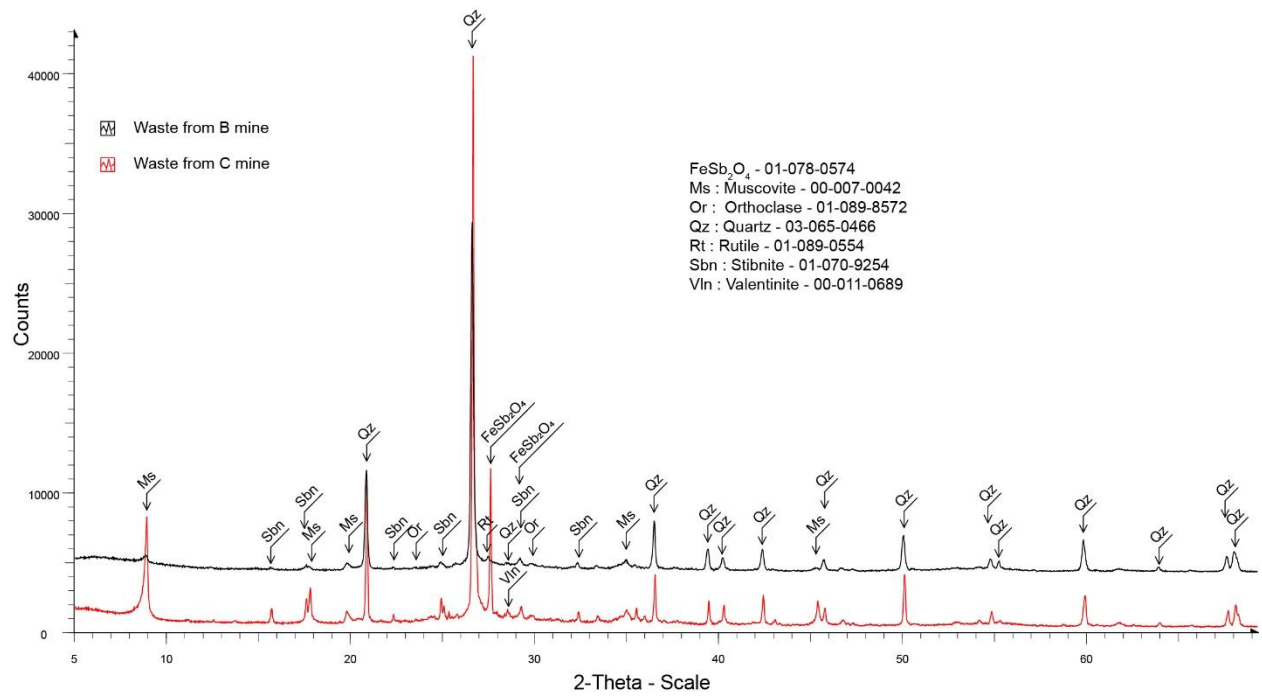


Figure 2. XRD of antimony mine wastes *Note to the publisher: two columns width*

## Microstructure and phase composition of clinker doped with waste

The antimony-substituted clinkers show a less developed microstructure than the one of the reference clinker; namely, cementitious phases are less identifiable (Figure 3). As for the interstitial phase, it appears much less developed than that of the reference clinker.

In both cases (B & C mine wastes), partly reacted remnants of metallic phases have been observed as inclusions in the ALITE (Figure 3). They are typically round, really bright in BSE mode, their diameter ranging from less than 1 micrometer to ca. 3 micrometers maximum. They are irregularly distributed through the sample; in places where they are present they form a constellation of droplets. Considering the size of the electron/matter interaction zone, their EDS analysis is only qualitative and concerns also their host phase.

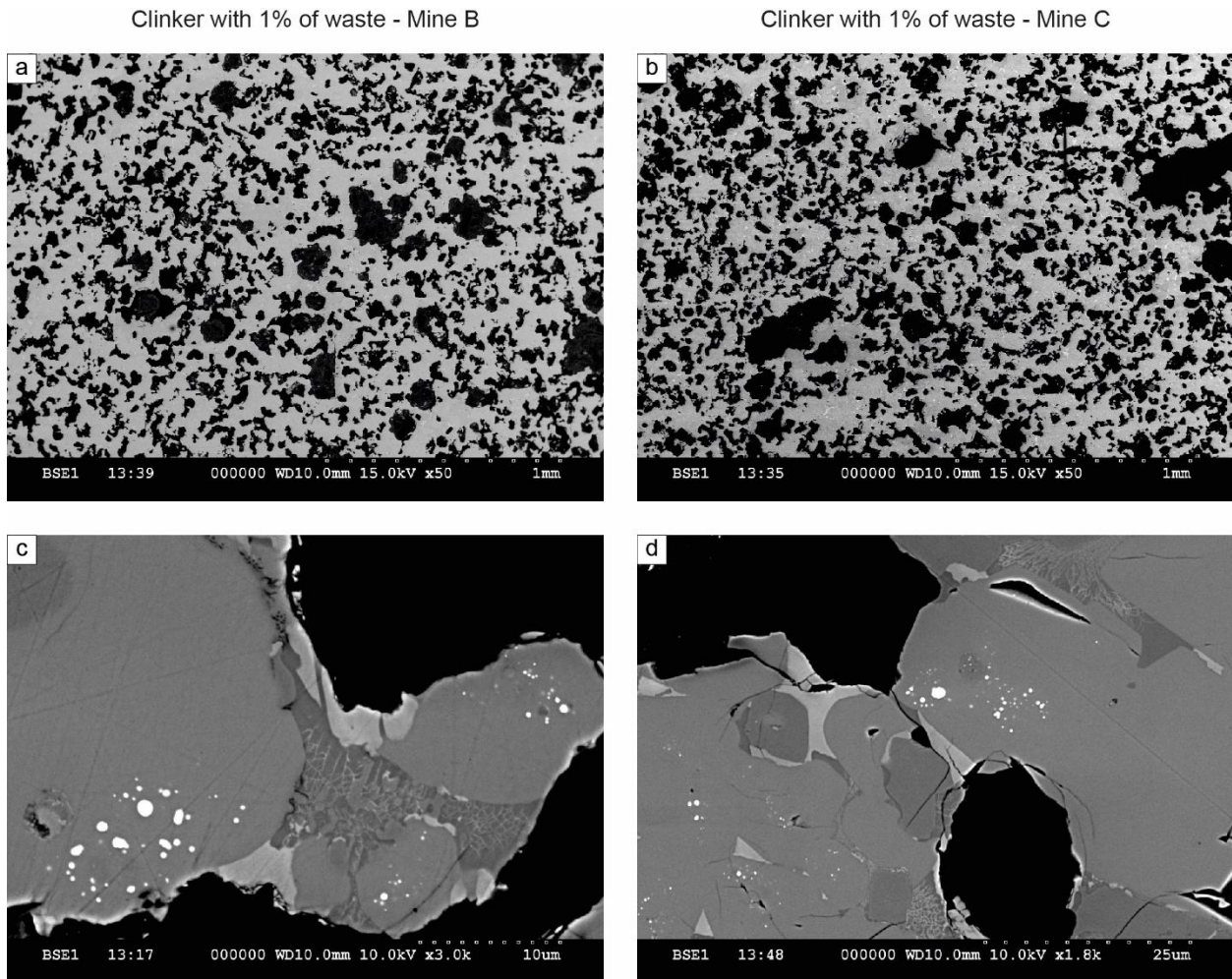


Figure 3. Microscopic features of clinkers doped with 1% of mining wastes B & C. a & b: general aspect of clinker. c & d: metallic inclusions in belite. *Note to the publisher: two columns width*

The shape of EDS spectra (Figure 4) highlights the typical difficulties encountered during the microanalysis in those waste-doped clinkers. Indeed, the bright spots (Figure 3), when directly analyzed, are too small and the electron-matter interaction zone accounts for an analysis of their matrix. In belite (Figure 4b), if Sb is present in low amounts, it will be hidden by the important Ca peak. In  $C_4AF$  (Figure 4c&d) the same problem is encountered.

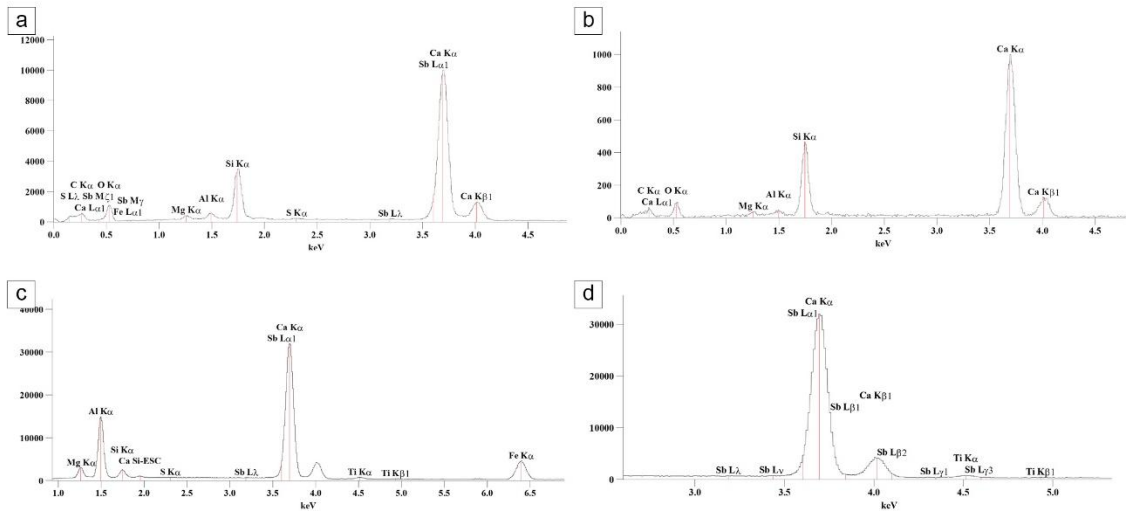


Figure 4. EDS spectra illustrating the Ca-Sb lines overlaps. a: analysis of a bright dot within a calcium silicate, b: analysis of a calcium silicate, c: analysis of a  $C_4AF$ , d: close-up view of the Ca peak for a  $C_4AF$  analysis. **Note to the publisher: two columns width**

The EDS analysis of the silicates reveals very low concentrations of metallic impurities, for example 0,6% of Sb, less than 0.1 wt. % of Cr and Fe in a ALITE from a clinker made with 1% of C waste (Figure 4). For this clinker, EDS analysis also reveals the incorporation of 0.4 wt.% of S, 0.4 wt.% of Ti and 0.2 wt. % of Cr in the interstitial phase, with a notable 3 wt. % of Sb.

The presence of Cr is problematic since the raw feed does not contain any amount of this element (Table 1). It is hence likely that this represents a sum peak, also known as pile-up peak 25–27.

Moreover, considering that standardless EDS analysis are normalized to a 100% total and also considering the overlaps of several lines between Ca and Sb, as well as the aforementioned possibility of sum peaks, WDS analyses have been carried out to give a better description of the phases formed. In order to test the method, spot analyses have been carried out on rounded, bright inclusions such as the ones presented in Figure 3. The spectral result is presented in Figure 5. It clearly shows that despite the closeness of their lines, Ca and Sb can be discriminated confidently, acknowledging the fact that analytical points have to be carefully selected with respect to the electron-matter interaction zone size. Namely, all points analyzed here have been selected far from a bright inclusion (Figure 3).

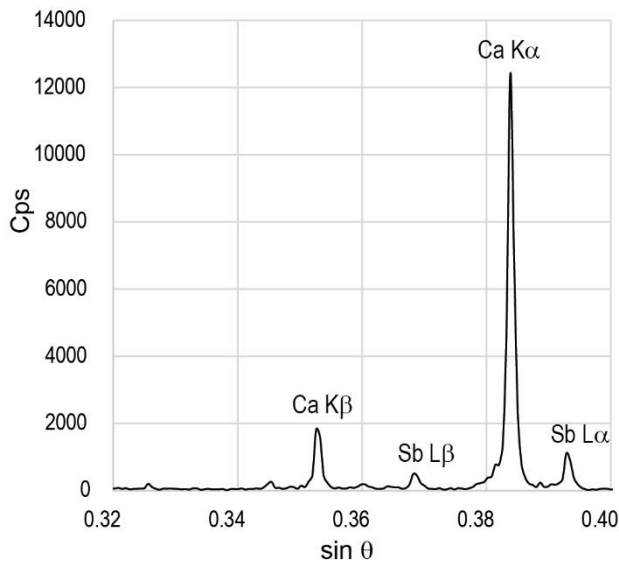


Figure 5. Extracted spectra from the LPET spectrometer showing the closeness of the Ca and Sb lines as well as their resolution in WDS. *Note to the publisher: one column width*

		DataSet/Point	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	Total	
	C4AF	1 / 1 .	3,49	18,95	3,75	0,01	45,31	1,11	20,19	1,61	0,07	94,4807	
CP1B		2 / 1 .	3,52	19,19	3,81	0,04	45,79	1,07	20,26	1,54	0,14	95,3538	
		3 / 1 .	3,89	16,63	3,83	0,05	45,22	1,25	20,38	1,91	0,10	93,2607	
		4 / 1 .	3,89	18,34	3,20	0,04	44,94	1,14	20,75	2,03	0,18	94,5099	
		5 / 1 .	3,93	18,26	3,34	0,01	44,91	1,12	20,26	2,03	0,22	94,0713	
		8 / 1 .	3,36	19,42	3,38	0,04	46,78	1,09	18,92	1,90	0,18	95,0896	
		17 / 1 .	2,83	18,43	4,94	0,03	46,60	0,86	19,66	1,43	-0,21	94,5849	
		C3A	6 / 1 .	0,82	29,69	2,75	0,03	54,65	0,08	5,50	0,43	-0,08	93,8675
			12 / 1 .	0,34	31,04	2,88	0,02	57,35	0,05	3,93	0,23	0,00	95,8437
		15 / 1 .	0,94	30,80	2,70	0,02	54,92	0,06	4,74	0,25	-0,21	94,2057	
		16 / 1 .	1,08	28,13	3,12	0,01	54,81	0,43	6,54	0,94	0,10	95,1642	
	C2S	10 / 1 .	0,31	1,89	29,70	0,50	60,39	0,24	0,94	0,40	-0,05	94,3242	
		13 / 1 .	0,08	1,05	31,20	0,08	61,31	0,35	0,50	0,34	0,07	94,9835	
	C3S	7 / 1 .	1,03	0,86	24,07	0,07	67,26	0,18	0,65	0,29	0,13	94,5428	
		14 / 1 .	1,08	1,12	24,00	0,10	67,00	0,21	0,66	0,30	-0,21	94,2631	
	Inclusion	9 / 1 .	2,00	9,16	3,86	0,94	49,94	0,41	3,13	22,00	0,24	91,6765	
		11 / 1 .	2,03	4,80	8,80	0,92	52,50	0,33	2,57	22,47	0,16	94,5675	

			MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	Total	
CP1C	C4AF	18 / 1 .	3,29	19,65	2,49	0,05	45,38	1,17	19,97	2,04	-0,14	93,8953	
		19 / 1 .	3,36	18,82	4,68	0,02	46,11	1,28	19,35	2,02	0,00	95,6406	
		20 / 1 .	3,46	17,91	3,35	0,03	45,56	1,43	19,64	2,51	0,02	93,8902	
		C2S	21 / 1 .	0,20	5,73	27,36	0,13	60,73	0,16	0,81	0,31	0,18	95,6039
			23 / 1 .	0,44	1,76	29,88	0,44	60,82	0,25	1,01	0,31	-0,30	94,6019
			24 / 1 .	0,38	1,72	29,75	0,49	61,33	0,25	1,04	0,32	0,00	95,283
			25 / 1 .	0,25	1,58	29,97	0,31	61,01	0,26	0,91	0,29	-0,06	94,5177
			26 / 1 .	0,36	1,69	29,93	0,36	61,34	0,23	1,00	0,27	0,05	95,2296
			27 / 1 .	0,40	1,77	29,71	0,43	60,84	0,24	0,96	0,33	0,08	94,774
			34 / 1 .	0,83	1,50	29,44	0,36	62,00	0,27	0,79	0,32	0,23	95,7332
			22 / 1 .	1,05	0,82	24,11	0,01	68,19	0,17	0,55	0,30	-0,14	95,0587
		C3S	28 / 1 .	0,93	0,77	23,90	0,03	68,13	0,13	0,59	0,31	-0,12	94,6822
			35 / 1 .	0,90	0,84	24,38	0,02	69,18	0,15	0,52	0,28	0,09	96,3618
			36 / 1 .	0,85	0,83	24,27	0,03	69,30	0,16	0,55	0,26	-0,09	96,1722
			37 / 1 .	0,81	0,85	24,20	0,06	69,15	0,14	0,57	0,27	-0,07	95,9685
			38 / 1 .	0,92	0,85	24,44	0,07	69,16	0,12	0,60	0,33	0,09	96,5748

Table 2. WDS results in wt.% for individual phases of the clinker.

All WDS results are presented in Table 2. For **calcium silicates**, the results are coherent both within belite and alite as well as within the two different wastes. The  $\text{Sb}_2\text{O}_3$  content ranges from 0.22 % up to 0.40 %. For the **C<sub>4</sub>AF** however the  $\text{Sb}_2\text{O}_3$  content is much higher (and still coherent within the two samples): it ranges from 1.42 % to 2.50 %. In **C<sub>3</sub>A**, which have been analyzed only in the CP1B sample, the  $\text{Sb}_2\text{O}_3$  content is much lower, ranging from 0.22 % to 0.43 %. Finally, the **bright inclusions** are rich (22%) in Sb, within a calcium silicate matrix. Their small size, compared to the electron-matter interaction zone, does not allow to have an analyze which characterize them correctly but rather gives an estimation. Finally, whereas the present paper is focused on Sb, it is worth noting that the trend for  $\text{As}_2\text{O}_3$  is unclear, being absent within most analyses but sometimes present in similar concentrations in both belite, alite and **C<sub>4</sub>AF**.

## 4 DISCUSSION AND CONCLUSIONS

The goal of this research is to incorporate the metallic elements found in high concentrations in mining wastes rich in antimony by partial replacement of the clinker raw material. The primary objective is to valorize the residues and minimize the risks of pollution that may occur as a result of the mining activity.

Elements such as S is known to affect positively the burnability of a Portland clinker<sup>28</sup>, which means that it minimizes the free lime content<sup>29</sup>. The same observation has been done when adding a wolframite-stibnite ore to the raw feed<sup>7</sup>.

In the present study, Portland clinker synthesized with as little as 1% of mining wastes rich in Sb and S (i.e. bearing metallic sulfides typical from such materials) already show a microstructure which differs from what is expected in a regular clinker. The chemistry of the phases is strongly influenced by the waste input in the raw feed and their content in foreign elements is likely to strongly affect their reactivity. Sulfur, for instance, is present in both belite and alite from the present study; it is known **to enhance belite hydraulicity**<sup>30</sup>.

The preservation of metallic phases as inclusions in the clinker's silicate show that they are not totally incorporated, however, their round shape indicates a partial reaction during the growth of the phases. The EDS analysis of the silicates reveals very low concentrations of metallic impurities, which is in good agreement with the low amount of mine waste added to the raw feed.

It is very likely that even smaller droplets of metallic phases, undecipherable under the SEM in polished cross-section, are present as inclusions inside the clinker's phases, and not as foreign elements incorporated in their structure. Considering the diameter of the interaction zone in the



clinker phases, typically around 5 micrometers <sup>31</sup>, smaller inclusions will not be analyzed as such and the analyzed volume will not be representative of a phase composition (Figure 6).

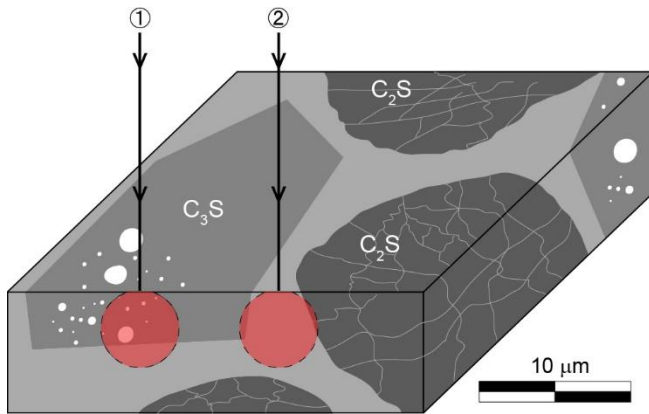


Figure 6. Schematic sketch of a doped clinker. Dark grey: belite, lighter grey: alite (prismatic shape), light grey: interstitial phase, white: metallic inclusions. 1 and 2 are electronic paths represented with their interaction zone. X-rays generated under the path 1 will stand for both alite, metallic inclusions and interstitial phase. X-rays generated under the path 2 will stand for both interstitial phase, alite and belite. **Note to the publisher: one column width**

Hence, the bright rounded inclusions (Figure 3), rich in Sb (Table 2) cannot be correctly analyzed. Within the context, it is not unlikely that a high temperature calcium antimonate phase such as Ca<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub> forms. This one is known in Ca-Sb bearing archeologic glasses and has been synthesized by firing a CaCO<sub>3</sub>-Sb<sub>2</sub>O<sub>3</sub> mixture at 1100°C <sup>32</sup>, coherent with the present high temperature context.

In order to study the long-term stability of metals and their effect on cement applications, it is necessary to conduct mechanical tests, durability tests, and leaching tests on cements derived from these clinkers obtained after substitution of metal mine residues.

**Also, although preliminary and exploratory, the present study also raises interrogations for the end-of-life of potential concretes which would be made with a waste-based clinker. Considering the minor amount of foreign ions incorporated into the clinker, which will be highly diluted**

within the sand and gravels of concrete, the Sb (for example) content will be even lowered compared to its initial incorporation. However, it will have to be considered depending on what will happen afterwards: deposition or re-use of the concrete? This point concerns all concrete produced nowadays with the incorporation of wastes.

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