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IMMOBILIZATION OF ARSENIC FROM COPPER SMELTER WASTE

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Abstract

Arsenic is an inconvenient impurity for copper smelters and its problematic its bound to worsen as concentrates become dirtier. Air emissions are prevented during the off-gas treatment so it deports to liquid effluents and dusts. From effluents it cannot be removed easily together with other metals and specific removal needs to be considered. At industrial level the preferred choice is precipitation and copper smelters thus seek precipitates that are safe enough for inexpensive landfill disposal.

The literature review identified the most common methods used by industry as well as more novel proposals to remove arsenic from solution. When precipitates or other types of solids are still too hazardous for safe disposal, it is possible to stabilise them with other methods discussed.

The experimental work tested one solid stabilisation approach, vitrification, on hazardous copper smelter waste. Next, after producing an arsenic-bearing solution similar to copper smelter effluents by leaching the same waste, five precipitation methods were tested: high-iron arsenical ferrihydrite, a two-step process using aluminium and iron, arsenate hydroxyapatite, gypsum-seeded scorodite and ferrous arsenate (symplesite). The short term leaching behaviour of the solids was tested with 24-hour bottle tests performed at different pH conditions.

The results showed that all methods produced solids somewhat safer than the original one, but only the symplesite and two-step precipitation methods have resulted in solids safe enough for landfill disposal. A preliminary cost estimation shows that these methods could be competitive with existing processes, while producing a safer solid. Regarding vitrification of the current waste, even though the particular conditions of the test were unable to produce a safe enough solid, the waste proved amenable to the process.

Keywords arsenic removal, copper smelter waste, arsenic precipitation, immobilization, vitrification

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Madrid, 8 August, 2016

Carlos Suárez García

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1 Arsenic in copper smelter waste

1.1 Introduction

The metals industry faces increasing pressure around the world to reduce the adverse impacts of its operations. In particular, copper smelters that process arsenic-bearing concentrates find themselves having great difficulties to meet the challenge of preventing arsenic emissions to the atmosphere, removing it from discharged effluents and producing a final safe waste that could be disposed inexpensively.

There are good reasons to be concerned by the fate of arsenic from copper smelters. The World Health Organization (WHO) has placed arsenic amongst the "top 10 chemicals of public concern" (WHO, 2010). Exposition to large doses is poisonous to humans, animals and plants and prolonged exposition to small doses of As is related to cancer and a wide number of other conditions (Kartinen Jr. and Martin, 1995; WHO, 2010). One of the most famous instances may be the case of Bangladesh. In that country a 70% mortality increase has been linked to drinking water with high As contents (above 150 µg/l) (Chakraborti et al., 2015; Uddin and Huda, 2011).

In order for As not to be uncontrolledly discharged and to meet the legal requirements, smelters need to remove almost all arsenic and the resulting solids must be safe enough for long-term storage. Ideally, this stable and insoluble form would be acceptable at non-hazardous landfills while having a high As loading, reducing disposal and transport costs.

Arsenic is not easily removed by the conventional methods used for other toxic metals, so specific considerations need to be made at copper smelters. The auriferous Giant Mine (Canada) is one example of the failure to address the long-term considerations of As-containing metallurgical waste. The processing included roasting of arsenopyrite to liberate gold. Arsenic trioxide was formed and collected as dust by cooling the off-gases. This way, 236 000 metric tons of dust were produced and stored underground (Riveros et al., 2001).

Long after the mine was closed, the poor storage conditions of soluble As_2O_3 led to the polluting of water sources, including several lakes (Derghazarian, 2011). To prevent further contamination, it was only in 2014 that a long-term solution was approved. It included permanently freezing the dust at a cost of almost one billion dollars for Canadian taxpayers ("Giant headache," 2014).

There are other examples of uncontrolled disposal of arsenolite (arsenic trioxide) leading to contamination, for example in Mexico (Carrillo-Chávez et al., 2000) or in New Zealand (Haffert and Craw, 2008). Not surprisingly, the industry has looked for arsenic compounds that will not cause the same problems and that, ideally, could be safely disposed of in a landfill together with other types of waste.

The structure of the work is as follows. This chapter discusses the problems arsenic poses to copper smelters due to its chemistry, presence in waste products and legal requirements. The following two chapters present the results of the literature review on methods for the removal of As from solution and the stabilisation of solids. Chapter 4 summarises the main

findings from the literature review and justifies the choice of methods used in the later testwork.

Hazardous waste generated in a copper smelter was used as raw material for the testwork described in chapter 5. The goal was to find an alternative to the current treatment that would result in waste acceptable at landfills. The different alternatives were compared based on their As immobilization performance, the concentration of arsenic they can carry and their leaching behaviour at pH relevant for landfills. The findings are discussed in chapter 6 and the conclusions can be found in chapter 7.

1.2 Chemistry of arsenic

Arsenic is a metalloid of atomic number 33 and atomic weight 74.9. It is one of the so-called toxic heavy metals. It belongs to group 15 in the periodic table, together with, for example, phosphorus and antimony, and some of its toxicity issues arise from the similarities with phosphorus.

In nature, arsenic can be found as sulfide minerals such as orpiment (As_2S_3) and realgar (As_4S_4), already identified by ancient Greece scholars due to their bright colours (Flora, 2014). Other sulfides of high importance for metallurgy are minerals like arsenopyrite (FeAsS), enargite (Cu_3AsS_4) or tennantite ($Cu_{12}As_4S_{13}$).

Natural weathering or industrial roasting of sulfides, lead to the production of arsenic trioxide As_2O_3, which depending on the lattice structure, is known as claudetite (monoclinic) or arsenolite (cubic) (Flora, 2014). This is a very volatile substance that sublimates at 135ºC under atmospheric pressure (Grund et al., 2000). As_2S_3 can also be formed by roasting, and is also able to sublimate easily, to a vapour phase of As_4S_6 at temperatures lower than its 320ºC melting point (Greenwood and Earnshaw, 2012).

One of the biggest concerns with toxic metals, including arsenic, is their solution chemistry. It will determine their mobility and potential to reach water sources, and can also be used for their removal. Figure 1 and Figure 2 summarise some of the issues specific to arsenic when compared to other toxic heavy metals.

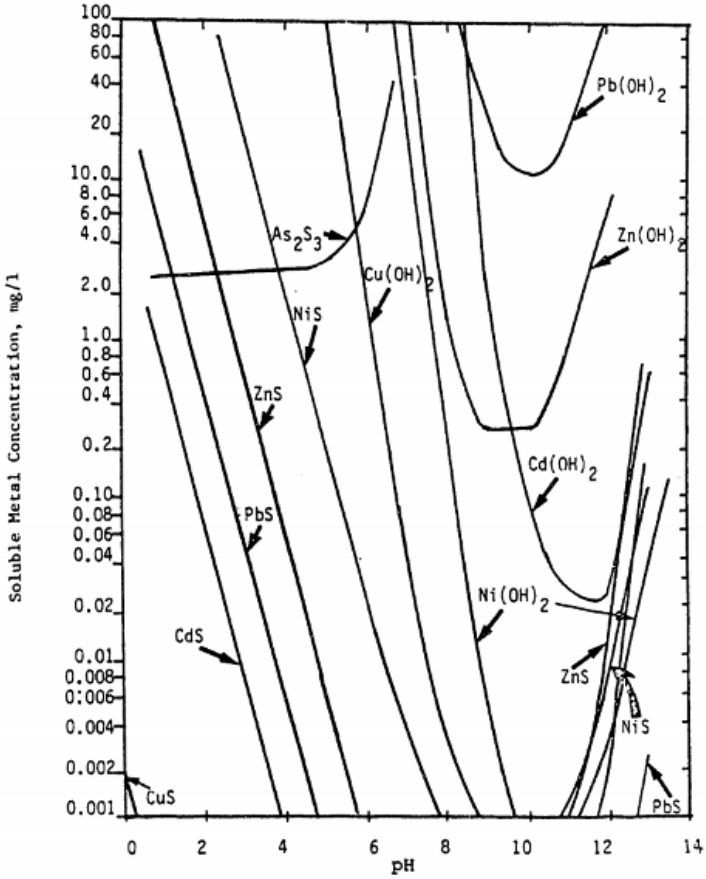


Figure 1. Solubilities of metal hydroxides and sulfides, copied from (Peters and Shem, 1993)

Figure 1 shows that hydroxides and sulfides of heavy metals such as Cu, Cd, Zn or Pb can be precipitated relatively easy by increasing the pH (usually via lime addition) which allows them to be separated via coagulation/flocculation and filtration or other solid/liquid separation methods (USEPA, 1980; Wang et al., 2005).

In contrast, unlike those heavy metals, arsenic does not form hydroxides, forming instead soluble oxyanions, as summarised in Figure 2, which presents (left) one Pourbaix diagram obtained for the As-O-H system. There are other versions with some variations, but this one was the most updated and care had been taken to use consistent data, according to its authors Lu and Zhu (2010).

Under reductive conditions arsenite (As(III)) species predominate: arseneous acid, H_3AsO_3, at low pH and the oxyanion $H_2AsO_3^-$ with increasing pH. Ground waters, usually reducing, will thus have higher arsenite concentration. Under more oxidising conditions like those of surface waters, there are arsenate (As(V)) species which are mostly ionic: arsenic acid H_3AsO_4 gives way to oxyanions $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} with increasing pH.

Other oxyanion-forming heavy metals: e.g. selenium or chromium, can be reduced to solid elemental Se (see Figure 2) and Cr_2O_3, respectively. Arsenic remains in soluble forms under all but the most reducing conditions (Flora, 2014), which may also lead to the formation of poisonous AsH_3 gas, arsine (Grund et al., 2000).

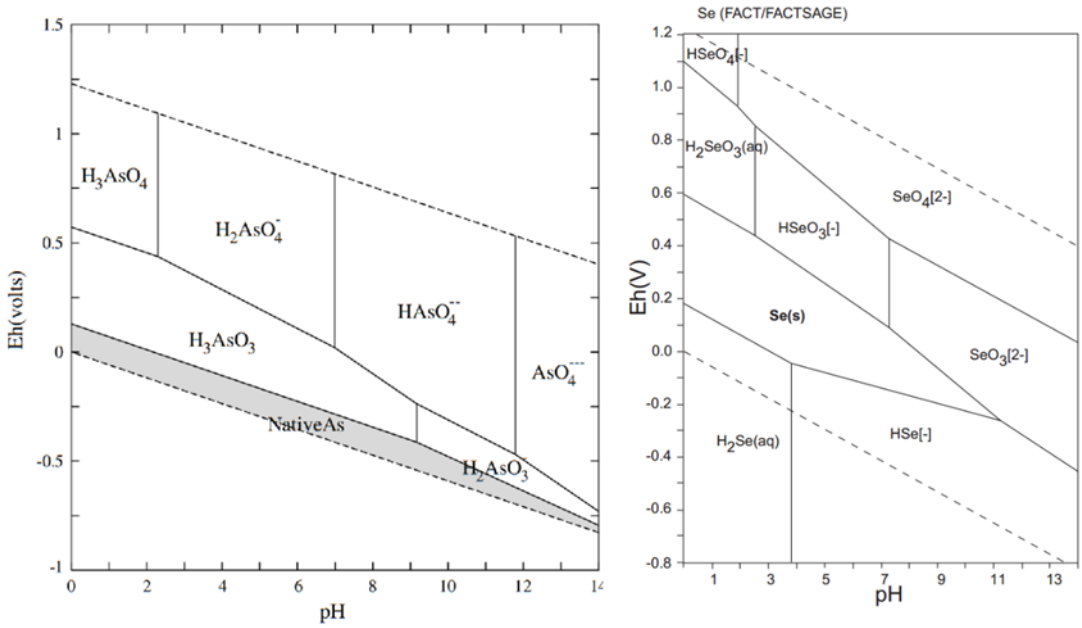


Figure 2. Eh-pH diagram for As-O-H system at 25ºC and 1 bar. Total As = 10-6 mol/L. Copied from (Lu and Zhu, 2010). On the right, the Se-O-H at total Se = 10-10 mol/L, for comparison, copied from (Takeno, 2005).

Arsenic metal is thus highly soluble in surface or most usual ground waters and so are arsenic oxides arsenolite/claudetite. The solubility of arsenolite in pure water at temperatures from 20 to 30ºC is reported at 0.207 mol As/kg H_2O (Bowell et al., 2014), or up to 16 g/l (Drahota and Filippi, 2009) . Islam et al., (2013) performed a leaching test with groundwater in which metallic As and arsenolite were readily dissolved resulting in leachate concentrations of respectively 4538 and 4240 mg/l after one year. According to (Vink, 1996), unless it is under very reducing conditions and at high arsenic activity in solution ($10^{-0.8}$ molal or 11.9 g/l water) it is not possible to have stable arsenic oxides. This is the reason why disposed arsenolite eventually dissolves and high arsenic levels are reported.

Moreover, Figure 1 shows that arsenic sulfide As_2S_3 is also soluble, especially in the pH range where other metals can be removed by forming sulfides. This was also corroborated in the study by Islam et al. (2013), reporting an arsenic release after one year of 653 mg/l for As_2S_3 and 319 mg/l for As_4S_4 sulfides.

The oxidation state of arsenic is important as As(V) compounds are seemingly less soluble than those of As(III), considered more mobile and toxic (Pal, 2015; Riveros et al., 2001). The charged or uncharged nature of the compounds also has relevant implications for their mobility. For example, ionic arsenate forms interact electrostatically, which leads to faster adsorption or ion exchange, compared to arsenite, only adsorbed via complexation. Also of importance is that pH changes in surface charge may lead to release of electrostatically adsorbed arsenate, and arsenates will find competition for adsorption sites from similar charged ions like phosphate and sulfate (PO_4^{3-}, SO_4^{2-}) (Flora, 2014).

The uncommon behaviour of arsenic compounds, both in solution and as volatile solids, helps to explain the relative difficulty in managing arsenic.

1.3 Arsenic in copper mining

Arsenic is commonly found in sulfide deposits of great relevance for the mining and metals industry, which are in fact the main producers of this metalloid (Grund et al., 2000; Riveros et al., 2001). Notably, copper and arsenic are found together in minerals such as enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$). These minerals are originated in epithermal deposits and are also commonly associated with gold and silver. That was the case of El Indio deposit (Chile), which was mined for over two decades (Filippou et al., 2007). It is only one example of how these arsenic-containing minerals become part of ore deposits and how As reports to metallurgical processes.

Arsenic compounds have some applications. In metallic form, arsenic is used in small quantities for alloying, with lead to produce car batteries and with copper (up to 0.3%) to improve corrosion properties. Another important application is in semiconductor materials, as gallium arsenide (GaAs).

Unfortunately, those applications do not demand large amounts. In fact, in the year 2000, 87% of the arsenic in end-products was being used for wood preservatives (Valenzuela, 2000). It became increasingly controversial to use toxic arsenic for those applications so they have been discontinued from 2003 in developed countries (Directive 2003/2/EC, 2003; USGS, 2015), considerably reducing the demand for arsenic and making it usually not economically attractive to do anything but discard it as waste (Harris, 2003).

Traditionally, the issues arising from handling arsenic have meant that smelters place penalties on concentrates with more than 0.2% As and, above 0.5%, they may refuse them altogether ("Rejecting arsenic from copper ores," 2009). For miners, this has meant avoiding high arsenic containing ore deposits, or the high-As parts of their deposits (Baxter and Scriba, 2010; Filippou et al., 2007).

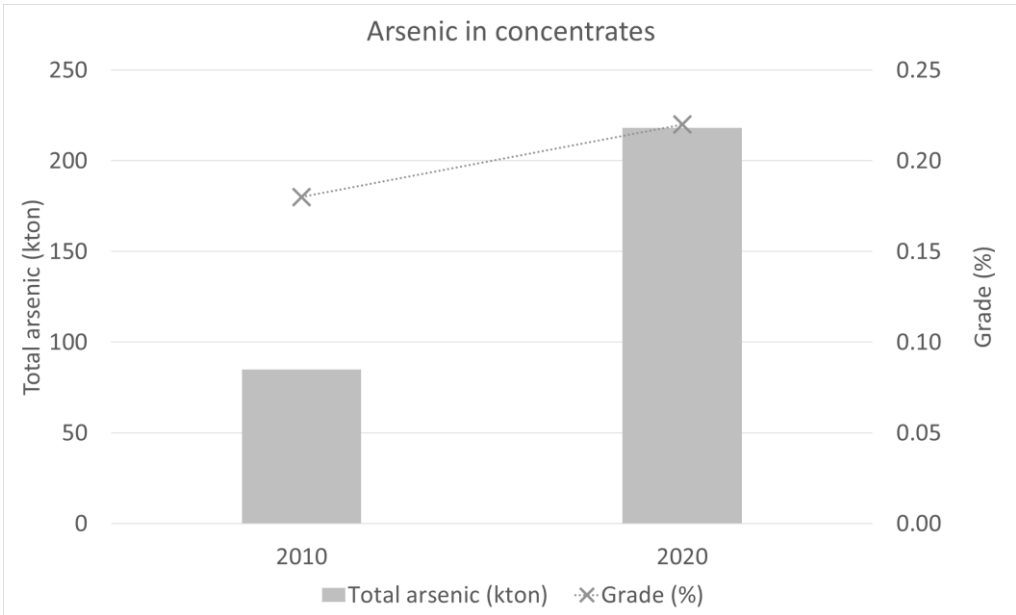


Figure 3. Estimates of arsenic produced and average global grade in concentrates (Mayhew et al., 2011).

As simpler orebodies deplete and only those with more complex mineralogy remain to be mined (Figure 3), this situation becomes increasingly problematic. For miners, avoiding As-rich orebody areas or trying to selectively remove As-rich minerals during processing is not so attractive, as As-Cu minerals become an essential component of the reserves. For smelters, even though higher treatment charges can be placed on dirty concentrates, blending high-As with low-As concentrates means large amounts of clean concentrates need to be available, something that is far from guaranteed in the future.

"*The key to the successful processing of arsenic-bearing minerals such as enargite is the ability to remove and stabilise As downstream*" (Safarzadeh et al., 2014), so it is important to determine what is the fate of arsenic in pyro and hydrometallurgical flow sheets.

1.4 Pyrometallurgical processing

A great majority of copper (80%) is produced by pyrometallurgical processing after a stage of concentration (Schlesinger et al., 2011). The general process can be seen in Figure 4: sulfide minerals are smelted to matte, which is then converted to blister copper and finally refined first into anode and then into cathode copper.

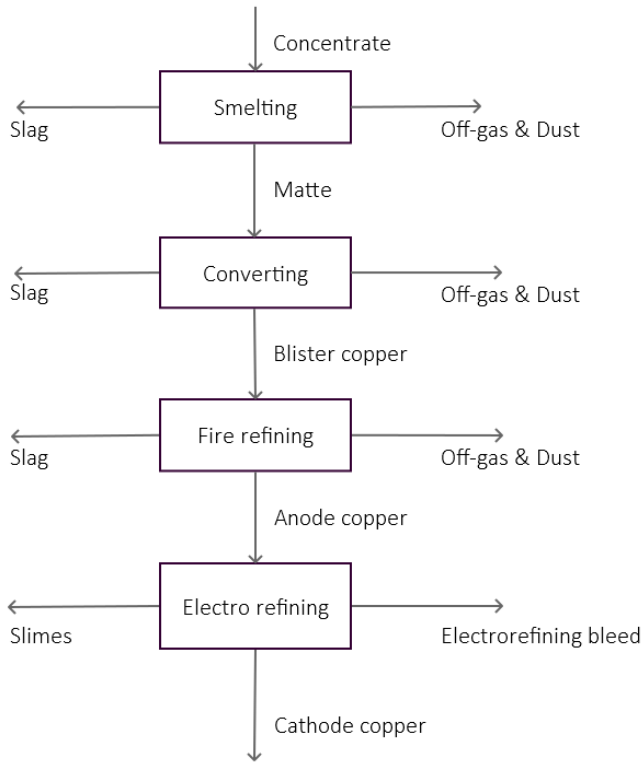


Figure 4. Pyrometallurgical processing of copper concentrates.

The fate of arsenic in such pyrometallurgical flow sheets was reviewed by Piret (1999). The high temperatures employed during the smelting and converting operations allow most arsenic to be volatilised as As_2S_3 and As_2O_3, whose emissions to the atmosphere are highly restricted around the world (Henke, 2009). The typical distribution of As is as shown in Table 1, based on the figures provided by several sources (Alguacil et al., 1996; Schlesinger et al., 2011).

Table 1. Distribution of arsenic during smelting (excluding dust).

	Matte	Slag	Off-gas
As distribution %	10-20	10-20	60-80

The off-gas from smelting also contains SO_2, other gases and dust particles; so it is collected and treated, together with the gas from the converting, refining and/or slag treatment stages. The first gas treatment steps are as follows:

1. Cooling with a heat exchanger, drop out dust
2. Removal of solids in an electrostatic precipitator (ESP)
3. Gas scrubbing, i.e. quenching with water

As Piret explains, arsenic is mostly removed in the scrubbing section where it is absorbed in the resulting effluent, the so-called weak-acid. It is reused for cooling, but a fraction needs to be replaced by fresh water to prevent too high acid contents, producing the so-called acid plant blowdown, an effluent that needs treatment before discharge.

There is also a more or less large fraction that remains in the dust, which also contains up to 20% Cu. The traditional approach is to (at least partially) recycle dust to the furnace to avoid losing copper, but this also accumulates impurities such as arsenic, which could eventually raise As concentration over detrimental levels in the final copper product (Piret, 1999; Schlesinger et al., 2011).

Dust has relatively high solubility and Morales et al., (2010), for example, report a case in which water leaching led to 54% dissolution, making it a poor solid form for arsenic immobilization. There is the option, applied for example in Kennecott (US) or Chuquicamata (Chile), to treat dusts to separate arsenic (and other impurities) before recirculation by leaching (Schlesinger et al., 2011). This recovers copper without increasing As levels in the furnace, but still results in a high-As effluent that will require treatment to keep *"arsenic in a stable form for disposal"* (Schlesinger et al., 2011).

Slag is likely to be treated in a slag furnace to recover valuables, volatilising the remaining arsenic into the gas treatment system or producing dust that is rich in arsenic and low in Cu, thus being less amenable to be recirculated into the processing, needing disposal or treatment.

Arsenic that remains in the matte goes on to the fire refining and electrorefining stages. It can be removed from molten copper with adequate fluxes up to 90%. 700-760 g/t As remain in the anode and get dissolved in the electrolyte during electrorefining. It will mostly remain in solution, leading to accumulation (European IPPC Bureau, 2014). Arsenic content in the cathodes should be kept as low as possible, as arsenic hinders mechanical properties (Safarzadeh et al., 2014). To prevent As contents above 1 g/t in the cathodes, the electrolyte needs to be partially removed (electrolyte bleed) and fresh solution added. The As-containing electrolyte bleed effluent will need to be properly managed (Schlesinger et al., 2011).

A roasting pre-treatment step can be implemented, but arsenic will need to be absorbed to prevent air emissions and transformed into solids other than As_2O_3, as already mentioned.

It can be mentioned that gold mining and metallurgy face the problem of managing arsenic as well, although it has been less of a deterrent in that case, due to its higher value (Baxter

and Scriba, 2010). Arsenical gold ores processing can include roasting as well, with the same associated issues as in the case of copper. Alternatively, hydrometallurgical operations will perform leaching of sulfides to liberate gold prior to cyanidation. Arsenic will be dissolved as well, either at high pressure or at atmospheric conditions, leading to residues similar to those discussed here (Robins and Jayaweera, 1992).

Effluent treatment in European smelters

The smelters surveyed by the European IPPC Bureau (2014) combine some or all the following streams before treatment:

1. Weak acid
2. Electrolytic refining bleed
3. Wet scrubber water
4. Surface run off water
5. Cooling water

Arsenic will be a major component of some of these effluents, and also of any leachate produced during dust treatment. The electrolyte bleed may contain from 2 to 30 g/l of As (Schlesinger et al., 2011). One example of weak acid composition is shown in Table 2.

Table 2. Example of weak acid composition (European IPPC Bureau, 2014)

	Cu	Pb	As	Ni	Cd
mg/l	2100	2600	2200	7	110

Table 3 shows that arsenic concentration in these combined effluents is up to 10 g/l. European smelters report to successfully remove arsenic during the water treatment process down to discharge limits below 0.1 mg/l.

Table 3. Concentration of metals in waste water before treatment at several smelters (European IPPC Bureau, 2014)

	Cu	Pb	As	Ni	Cd	Zn
mg/l (maximum)	2900	4500	10000	4000	3100	5000
	2450	1000	10000	450	3100	4400
	2000	300	10000	4000	500	5000

The treatment most commonly reported by European smelters consists in neutralisation with milk of lime and with the use of flocculants and coagulants. This results in the production of clean gypsum first and a contaminated sludge at higher pH, which will contain most arsenic from the smelter in the form of calcium arsenate. This lime precipitation method and its issues are discussed in the next chapter.

1.5 Hydrometallurgical processes

Leaching and bioleaching processes will lead to the solubilisation of As due to its high mobility (Riveros et al., 2001). Once in solution, the same issues of arsenic removal and its proper fixing into stable solids as for smelter effluents need to be considered, so any successful approaches are thus relevant to those processes as well. Different conditions may be available, though, as hydrometallurgical processes at high pressure and

temperature have been proposed and would allow for the immobilization of arsenic in different ways.

Safarzadeh et al. (2014) or Baxter and Scriba (2010) thoroughly review a large number of hydrometallurgical options for high-As ores and concentrates, but not all of them detail how (or if) arsenic is immobilised. One example that does is the CESL copper process, a pressure leaching alternative for high-As ores and concentrates which advertises its arsenic immobilization approach (Mayhew et al., 2013). As will be mentioned in section 2.3, high pressure allows iron and arsenic to precipitate as scorodite, thus remaining as that solid in the leach residue. However, section 2.4 will discuss that it is not clear whether scorodite is the final solution to the arsenic problem.

The leaching of enargite is slow as it is one of the most refractory copper minerals. That is why high temperature (from 150 to 230ºC) and pressure processes have been proposed, which require autoclaves and the associated high capital investment. Atmospheric processes have been designed: Albion (around 100ºC leaching after high intensity grinding), Galvanox^{TM} (80ºC leaching using galvanic effect that selectively leaches Cu), HydroCopper (85-100ºC leaching in chloride medium) or bioleaching.

Given that the majority of copper is produced in pyrometallurgical operations the need for addressing the problems in smelter waste streams is urgent, even if alternative hydrometallurgical solutions may eventually become commonplace.

A mixed approach is to perform a hydrometallurgical pre-treatment step prior to smelting. This is the case of the Toowong Process (Core Group, 2016). Alkaline leaching is performed on dirty concentrates, so that only impurities such as arsenic are removed, while a solid residue containing Cu can be sold as clean concentrate to the smelter. The leachate effluent needs to be treated for the removal and immobilization of arsenic.

1.6 Disposal of arsenic-bearing waste

Due to its toxicity, countries have legislation regarding the maximum limits of arsenic in air, water and soils. For example, the World Health Organization has set 10 µg/l as the recommended limit for drinking water and it has been implemented among others through the European Union Drinking Water Directive, the US Chemical Contaminants Rule, or the Chilean Drinking Water Official Norm since 2006 (Chilean Health Ministry, 2006; Directive 98/83/EC, 1998; USEPA, 2002). There is also the mandate for European countries to control and reduce arsenic levels in surface waters (regulated by the Directive 2006/11/EC of the European Parliament (2006)) and in air (Air Quality Directive approved in 2008).

In the case of industrial operations such as metallurgical plants, according to the Industrial Emissions Directive (European Parliament, 2010) they need to, amongst other obligations: prevent the generation of waste, apply the best available techniques and prevent (or cause no significant amounts of) pollution. Thus they have to ensure that emissions of substances such as arsenic to air and water are below target limits set by national authorities, so uncontrolled discharge of As-bearing liquid or gaseous effluents is not an option.

Smelters surveyed by the European IPPC Bureau, (2014) had to comply with maximum legal limits for the discharged effluents in the range of 0.1 to 0.3 mg/l As (on average), and

effluents may contain 20 000 times more arsenic originally. The limit could be less demanding in other parts of the world and, e.g., Piret (1999) reported a 1 mg/l limit for effluent discharge in the US at the time.

If it is successfully removed from solution, As becomes part of a contaminated sludge that needs disposal. For the landfilling of arsenic-bearing solids, as per the Landfill Directive (Council of the EU, 1999) the leachability of As and other toxic substances needs to be tested and compared against the limits for the landfill type, which can be seen in Table 4.

Table 4. Limits set by the 2003/33/EC Council Decision establishing criteria for the acceptance of waste at landfills, when using the EN 12457-4 24-hour batch test.

Landfill type	Inert	Non-hazardous	Hazardous
Maximum As leached (mg/kg dry mass)	0.5	2	25
mg/l for L/S = 10	*0.05*	*0.2*	*2.5*

The EU legislation allows for stable hazardous waste that meets the limits to be disposed of into non-hazardous landfills, whose fees are lower than those of non-hazardous landfills. For example, in Spain, one regional authority charges 25 to 47€ per tonne in non-hazardous landfills, whereas the fees for hazardous landfills go from 115 up to 406€ per tonne (Aragon regional government, 2016).

If the waste is not accepted in any kind of landfill, then producers will have to treat them until they do, or store it in their own monitored facilities, which would lead to even higher costs.

Therefore, copper smelters need to remove As from their effluents and find a safe disposal method in order to comply with legislation. This would also translate into lower disposal costs for smelters and thus an improved capability for processing high-As concentrates.

1.7 Evaluating arsenic mobility after disposal

As seen above, the key parameter studied to accept or reject waste into a landfill is its leaching behaviour, both in the US and the EU. From the previous discussion on the chemistry of arsenic it can be seen that it behaves differently from other toxic heavy metals. This has important consequences, as the screening tests that can more or less accurately predict the mobility other heavy metals are not so well suited to predict that of arsenic.

If the goal is to landfill the waste, leaching behaviour testing should take into account the conditions of the landfill. Non-hazardous, municipal solid waste (MSW) landfill leachates may reach high pH values with time (as the landfill becomes “mature”). The typical range is reported as pH 4.5 to 9, with matured municipal landfills stabilised above 7.5 (Baig et al., 1999; Umar et al., 2010). In the case of hazardous landfills, according to a US EPA report (Shuckrow et al., 1987), leachates from 6 different sites showed a range of pH from 6.3 to 7.9.

The most often reported test in the literature is the Toxicity Characteristic Leach Procedure (TCLP), the US standard screening test. It is performed at pH 5, and even though most heavy metals are readily soluble at that pH, the opposite is true for several of the solids used for As immobilization. Therefore, TCLP conditions are deemed unsuitable for estimating As mobility under actual landfill conditions, potentially underestimating the mobilisation of arsenic (Ghosh et al., 2004).

The EU legislation distinguishes between compliance and characterization tests. The standard compliance test in the EU uses water as lixiviant and the pH is allowed to evolve freely, so it may reach pH values irrelevant for landfill disposal. However, it is mandatory for any waste to be landfilled to first describe fully the influence of pH in the leaching behaviour with the EN 14429 so the results of a single condition test will not be the only parameter determining waste acceptance.

1.8 Thesis goals

The focus of the research has been on the immobilization of arsenic from copper smelter effluents such as the weak acid and electrolyte bleed, which usually results in the production of sludge that is hazardous and expensive to deal with. The reason is that the waste available for testwork came from one such process. Other types of waste such as flue dusts have not been directly considered for this work, but the conclusions may be applicable as well to effluents resulting from dust leaching.

Copper smelters face the challenge of having to process increasingly dirtier concentrates under tightening environmental regulations and poorer market conditions. Finding a cheap way to safely dispose arsenical waste is vital for smelters, more so as "*with the progress of time, increased environmental awareness and more stringent regulations are likely to impose more restrictions on disposal options*" (Pal, 2015, 271).

Studying this topic is relevant because, even though the problems associated with some old methods were recognised long ago (Twidwell and Mehta, 1985), no solution has been found yet that can be considered fully satisfactory in terms of cost and long-term stability. It is thus still thoroughly researched as shown, for example, by the amount of patent applications filed over the last 20 years which mention "scorodite" (Figure 5), one of the precipitates used for the immobilization of arsenic that will be discussed in the next chapter.

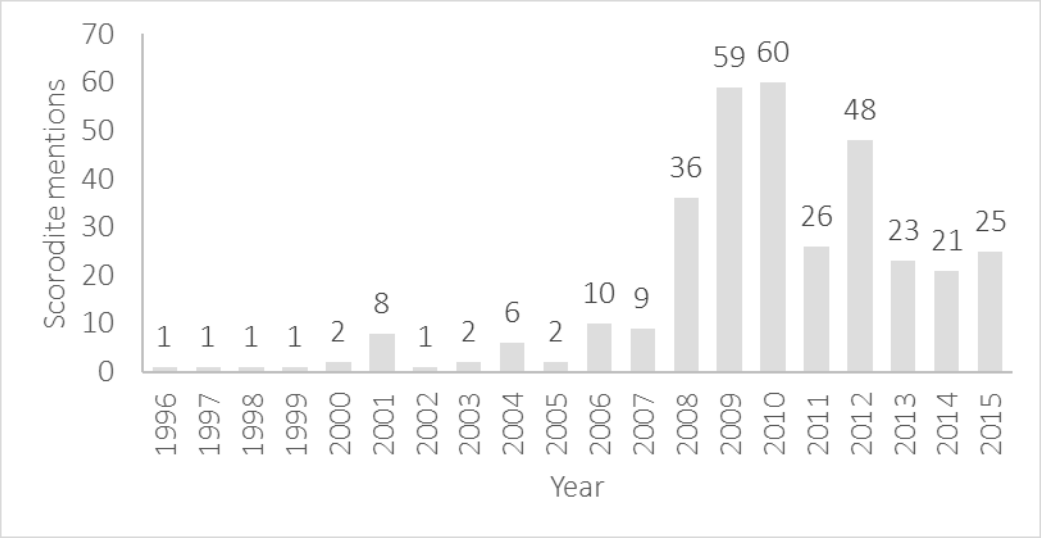


Figure 5. Patent applications that mention "scorodite" over the last 20 years. Results from the patent search engine The Lens.org.

Therefore, the aim of this research is to gain an understanding of the problematic of arsenic-bearing waste in the copper industry and identify solutions to reduce waste disposal costs, with specific goals to:

1. Explore and critically evaluate the alternatives, applied and proposed, to manage arsenic-bearing metallurgical waste streams.
2. Choose some of the most promising ones and test them on actual metallurgical waste.
3. Decide whether any of them are suitable to implement an alternative to the current process that would result in waste accepted at landfills.

2 Removal of arsenic from solution

2.1 Overview of treatment options

The first goal of treating copper smelter effluents is to remove toxic substances to levels below legal limits, thus producing a clean water stream that can be discharged into the environment safely. As mentioned, European smelters will usually need to reduce As levels below 0.1 mg/l.

There have been several reviews of the arsenic problem in the metallurgical industry and the issue of long-term safe storage of As-bearing waste, such as those by Valenzuela (2000), Riveros et al. (2001), Twidwell (2011) or Houngaloune et al. (2013).

2.1.1 Dilute effluents

The treatments methods of filtration, adsorption or ion exchange will be only briefly mentioned as they are mostly applicable to wastewaters with low arsenic concentrations. For example, the USEPA (2002) reports cases of successful application with feed wastewater As levels from less than 0.05 mg/l up to 3.8 mg/l.

These methods result in a residual high-As solid that needs to be treated or disposed of, or a concentrated liquid reject, which needs to be treated on its own anyway. Eventually, the only long-term solution that prevents any future contamination is for arsenic to be immobilised as a solid.

Membrane filtration

A semi-permeable barrier, membrane, can be used to remove certain constituents from contaminated water. Membrane processes that act mainly by physical sieving are appropriate only for As-containing particles. Dissolved arsenic species can only be removed by so-called nano-filtration or by reverse osmosis, which can separate molecular-size components. The oxidation state of As will be of importance, and pre-oxidation may be necessary as As (V) is more easily filtered (Pal, 2015).

The performance of membrane processes is hindered by other components of the solution/sludge, such as suspended and colloidal solids, as well as organic compounds, other high molecular weight dissolved solids, the pH and temperature (USEPA, 2002).

Membranes can remove not only As, but other contaminants as well, so they can be interesting for that reason. On the other hand, frequent replacement of the membranes is necessary due to fouling, which also leads to relatively low water flux, at least in the most commonly used designs (Pal, 2015).

Membrane filtration produces a clean water stream, but also a concentrated reject that needs to be managed. Pal et al. (2014) for example, present an integrated nanofiltration-coagulation system that stabilises the reject by precipitation, so it can be seen that the filtration step cannot, on its own, solve the problem of As waste stability.

Ion exchange

In this type of process, As-contaminated water is made to flow through a strong base resin. Ever since arsenic in solution is mainly in anionic form, arsenic anions will get exchanged with those adsorbed on the resin surface.

The products of ion exchange are a loaded exchange bed and the clean water. The loaded bed can be regenerated by a process of backwashing, regenerating with fresh solution and rinsing. The resulting products are an As-containing reject solution and clean water. The former will still need to be discarded, although with a fraction of the original volume, which can be very small. (USEPA, 2002).

Good performance of these types of systems requires several factors. Arsenic should be in oxidised state. A pH range of 6.5 to 9 is recommended and there should be low concentration of competing ions (such as sulfate), fouling agents and others like iron (III).

Adsorption

A number of different adsorption media can be used, in the form of a fixed bed through which the contaminated solution flows. Common adsorbents are: activated alumina, activated carbon, copper-zinc granules, different forms of iron oxides, greensands ($KMnO_4$-coated glauconite), surfactant-modified zeolite and other proprietary media (USEPA, 2002).

Some residues such as fly ash or red mud have also been used (Pal, 2015). Recently nanoparticles for arsenic removal from water have been the subject of much research, as shown by the number of reviews available (Lata and Samadder, 2016; Patil et al., 2016). Very high adsorption capabilities have been obtained due to their high surface area.

As in the case of ion exchange, the media will eventually be exhausted and will need to be regenerated or replaced. The spent media should be stable enough if it were to be directly disposed, and if it is regenerated instead, another treatment process for the residual waste solution should be implemented. It has been disappointing to find little mention of this issue in many of the articles.

2.1.2 Metallurgical effluents

The previous processes have several disadvantages that make them unsuitable as a solution for metallurgical effluents. First of all, they are well suited for effluents with relatively low As concentration (less than 5 mg/l) and readily applied to small and/or intermittent flows (Basu et al., 2013; Peters and Shem, 1993). For low-As effluents, large volumes of water can be treated before needing to replace o regenerate the solid media. For solutions with high concentrations of arsenic and when there are other competing ions in solution, such as sulfate, which "*strongly interfere with arsenate sorption*", precipitation is the preferred choice (Dambies, 2005; Leist et al., 2000).

Some other advantages of the previous processes when applied to other metals, including easy recovery from the reject solutions, are of no use for arsenic due to the lack of market (Wang et al., 2005). Therefore, the focus of this section will be on chemical precipitation methods for removing arsenic from solution. Chemical precipitation is amongst the Best Available Techniques recommended by the EU and was selected the Best Demonstrated

Available Technology (BDAT) by the USEPA for wastewaters in 1990 (Rosengrant and Fargo, 1990).

2.2 Oxidation of dissolved arsenic

Oxidation of arsenite to arsenate is a pre-treatment common to most immobilization processes. As mentioned, arsenic(V) is preferred as it is more easily removed due to its charge and as its compounds are less soluble (Sullivan et al., 2010).

Welham et al. (2000) had summarised the state of the art of arsenite oxidants by saying that an *"oxidant suitable for metallurgical use has yet to be reported"*. Indeed, it has been found that neither air nor oxygen are effective at low temperatures (Riveros et al., 2001). Proposed alternatives include H_2O_2, O_3, chlorine (via Cl_2, NaOCl, ClO_2), Fe(VI) compounds, manganese compounds (Mn-oxyhydroxides, $KMnO_4$, pyrolusite MnO_2 (Liu et al., 2012)) or SO_2/O_2 mixtures (Demopoulos, 1998).

Hydrogen peroxide, for example, has been reported as unsuitable by Welham et al. (2000) or Sorlini et al. (2010), at least at low temperatures and without any other modification. Sorlini et al. (2010) showed peroxide alone is ineffective for As oxidation: only a 3% oxidation yield was achieved when using 5 mg/l of H_2O_2 to oxidise an 0.1 mg/l arsenite solution. That is, a molar H_2O_2/As ratio above 100 was unable to produce a high yield of oxidation. Nevertheless, in the same study it proved much more effective when UV light is present and it is the oxidant of choice at the EcoMetales treatment plant (EcoMetales, 2014).

Sorlini and Gialdini (2010) showed that "*sodium hypochlorite and potassium permanganate are the best"* out of 4 reactants tested, which also included chlorine dioxide and monochloramine. $KMnO_4$ can be added at stoichiometric (molar: Mn/As = 2/3, as per Equation 1) ratios for low As concentration, but somewhat higher than stoichiometric if high levels of As need to be oxidised.

$$3H_3AsO_3 + 2MnO_4^- \rightarrow 3H_2AsO_4^- + 2MnO_2 + H_2O + H^+ \qquad \text{Equation 1}$$

Miranda (1996) also successfully used potassium permanganate $KMnO_4$ to oxidise a metallurgical effluent at 1.5 times the stoichiometric ratio. In both cases the original solution only had a concentration of As up to 0.3 mg/l, and almost 100% oxidation rate in under a minute was reached. Pal (2015) concluded that potassium permanganate is one of the safest options and cheaper than alternatives such as ozone or hydrogen peroxide.

2.3 Precipitation with iron

According to several authors, the most common method for removing arsenic from effluents is its precipitation/coprecipitation with iron (Majzlan et al., 2012; Riveros et al., 2001; USEPA, 2002). However, only one European smelter reports to use reaction with iron(III) as its As removal process (European IPPC Bureau, 2014).

There are several phases of iron and arsenic which may form when precipitating together from solution. The controlling factors are mainly temperature, Fe/As molar ratio and pH.

The resulting phases can be differentiated, amongst other properties, by their degrees of crystallinity.

Under uncontrolled ambient conditions, and depending on the Fe/As ratio, poorly crystalline phases are formed. According to Harris, in 2003 "*by far the most widely-practiced and accepted method used worldwide*" to remove As from solution was precipitation of arsenical ferrihydrite, one of those low temperature phases. High temperature and pressure lead to the precipitation of crystalline phases and, more recently, processes have been developed that can produce those crystalline phases under controlled atmospheric conditions.

2.3.1 Atmospheric precipitates

At room temperature and pressure, neutralization of As(V) and Fe(III) solutions will result in precipitation starting from around pH 3. The molar ratio Fe/As in solution should be larger than 4, and it can be as high as 20 in order to produce a solid that is safe enough (Miranda, 1996; Raghav, 2013).

Starting from Fe(III) solutions, two main types of ferrihydrite can be precipitated, differentiated by their X-ray diffraction response (shown in Figure 6) and which are in turn called 2-line or 6-line ferrihydrite. 2-line ferrihydrite forms by fast neutralization at room temperature and 6-line when higher temperatures are used. Precipitation can also be achieved by oxidation of Fe(II) solutions (Cornell and Schwertmann, 2003).

When solutions contain As as well, the precise nature of the precipitates has been a matter of debate. It has been thought that evidence supported the existence of a "basic ferric arsenate" compound of chemical formula $FeAsO_4 \cdot x\ Fe(OH)_3$ (Krause and Ettel, 1989), next that the precipitate is "ferrihydrite [$Fe(OH)_3$] containing strongly adsorbed arsenate" (Riveros et al., 2001) and more recently, that the precipitate is actually a physical mixture of ferrihydrite and ferric arsenate depending on the starting Fe/As ratio (Berre et al., 2007b; Paktunc et al., 2008). The adsorption mechanism is worse than coprecipitation, so that ideally the process should be "*precipitation of iron in the presence of arsenic*" and not iron precipitation followed by arsenic adsorption (Miranda, 1996).

Besides, the physical nature of the precipitates has been considered amorphous in the past, but Twidwell and Hohn (2005) say it is better described as nanocrystalline.

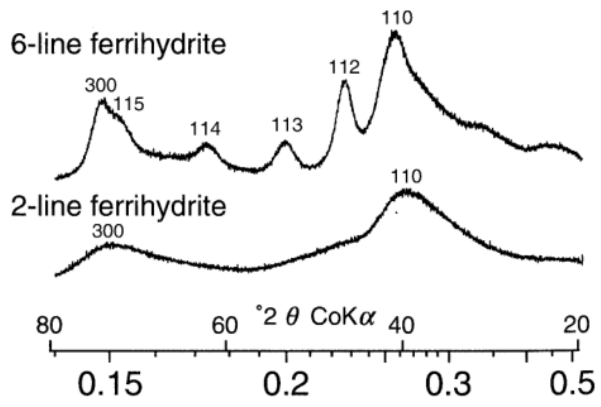


Figure 6. The X-ray diffractograms of 2-line and 6-line ferrihydrite, copied from Cornell and Schwertmann (2003).

Industrial neutralisation is usually performed with milk of lime, and it may in fact lead to more stable solids than using NaOH, as reported by Jia et al. (2012). Arsenic (III) gets removed less easily than As(V) so a pre-oxidation stage needs to be implemented if present.

The Fe/As molar ratio has a huge impact in the removal efficiency, as shown in Figure 7. Furthermore, higher Fe content in the precipitates also lowers As solubility of the resulting solids (Papassiopi et al., 1996).

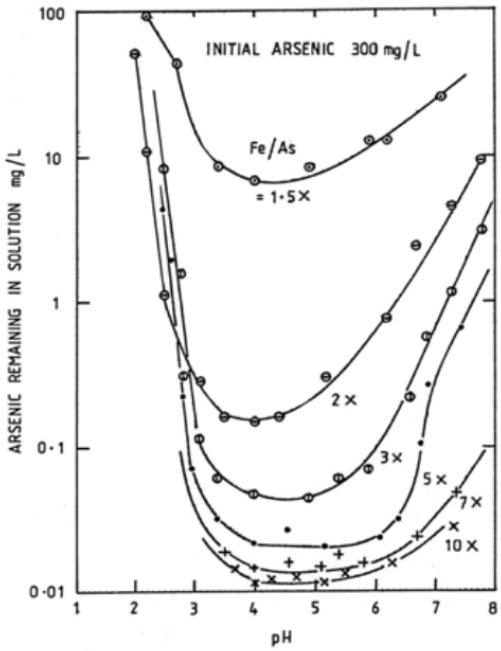


Figure 7. Removal efficiency as a function of pH and Fe/As molar ratio, from (Twidwell et al., 2005).

It has been found that atmospheric iron hydroxide precipitates are metastable and transform to goethite or hematite, controlled by pH and temperature (Welham et al., 2000). The conversion comes with a large change in surface area, which would release adsorbed arsenic.

This would mean that ferrihydrite is not a suitable candidate for the long-term storage of arsenic. The conversion, nevertheless, presents slow kinetics and a number of factors can change the speed of the reaction. Reducing conditions such as those produced by bacteria help in the transformation, but adsorbed ions help stabilise ferrihydrite, so arsenical ferrihydrite is in fact more stable than "regular" ferrihydrite (Wang et al., 2015).

This may explain how ferrihydrite/ferric arsenate precipitates are able to pass the standard TCLP test but it also shows their long-term stability may be compromised, especially depending on the particular disposal conditions (Twidwell and McCloskey, 2011; Welham et al., 2000).

2.3.2 Hydrothermal precipitation

The stability problems of arsenical ferrihydrite pushed for the research of alternatives. High temperature and pressure allow for crystalline iron arsenate phases to be formed, which have been shown to be less soluble (Monhemius and Swash, 1999). A widely

reported graph (Figure 8, in its last version by Drahota and Filippi, (2009)) shows the marked improvement in arsenic retention of crystalline scorodite compared to that of a ferric arsenate of the same 1:1 molar ratio.

It is important to note, though, that amorphous ferric arsenate is never produced in the industrial practice from a 1:1 ratio, and that much higher ratios are used, leading to more stable precipitates as mentioned in the previous section.

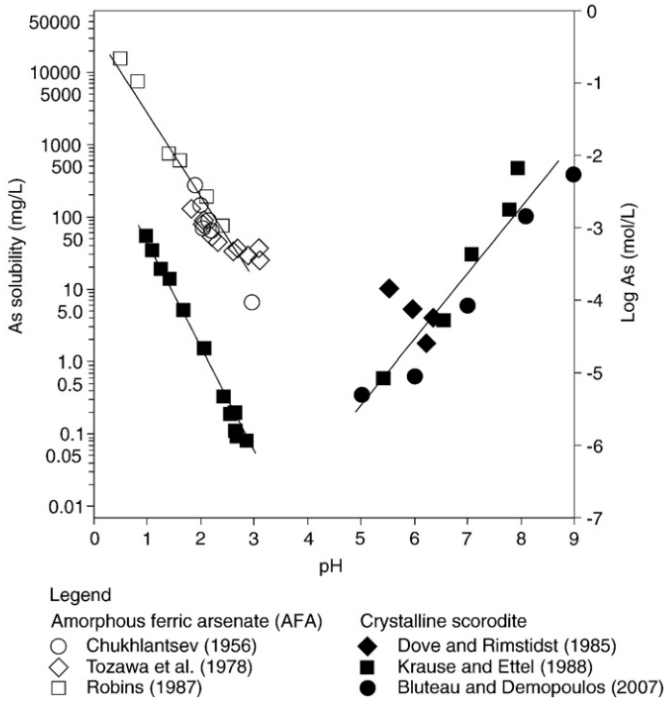


Figure 8. Solubility of amorphous arsenate and crystalline scorodite, both with Fe/As = 1, according to the results of different studies. Copied from Drahota and Filippi, (2009).

The production of crystalline ferric arsenate, scorodite ($FeAsO_4 \cdot 2H_2O$), presents some practical advantages over ferrihydrite coprecipitation: iron consumption is lower (if compared to high Fe/As precipitates), the solids contain more arsenic and dewatering is easier (Demopoulos, 2005). On the other hand, *"for the removal of small amounts of arsenic from acidic processing effluents"* Demopoulos still recommends the ferrihydrite/ferric arsenate precipitation from solutions with Fe(III)/As(V) molar ratios above 3 or 4, which has less demanding conditions.

Autoclave processing is a capital-intensive operation as high-pressure resistant vessels are required, as well as the associated infrastructure. This is why it can be more easily justified as a unit operation of gold processing than in the case of copper hydrometallurgy or the processing of waste from smelters.

Rigorous study of the precipitates formed at high T and P has led to the identification of several crystalline phases and not only scorodite. At least three studies done on the same temperature range have led to some differences in the phase identification (Dutrizac and Jambor, 2007; Gomez et al., 2011; Monhemius and Swash, 1999). The phases can have severely different solubilities, and thus this is a matter of relevance for their disposal.

The conclusions from the latest, Gomez et al. (2011), were that four main variables determine the formation of phases: temperature, Fe(III)/As(V) molar ratio, acidity and time, and they summarised their findings in Figure 9. Besides scorodite, it is possible to produce the FAsH and BFAS phases, which were equivalent to the type I and II phases reported by Swash and Monhemius (1995). The solubility of FAsH/type I was found to be the greatest of the phases studied, followed by BFAS and scorodite.

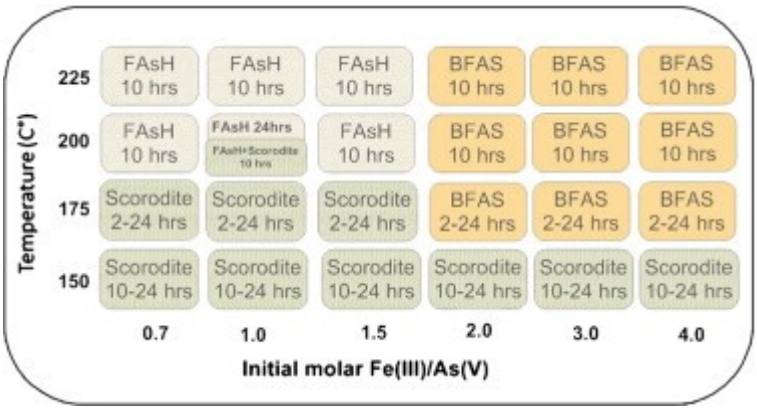


Figure 9. Phases formed by hydrothermal precipitation of iron and arsenic (Gomez et al., 2011).

In the same study Gomez et al. (2011) performed long-term bottle leaching tests on scorodite and the other phases, but all of them showed high arsenic release at pH above 7. Thus, their recommendation was that "*disposal of these phases should be done at pH ~ 7 or lower to avoid significant arsenic release"*, which is obviously at odds with the goal of producing waste that is suitable for landfilling, as has been discussed before.

2.3.3 Atmospheric scorodite

The possibility of producing crystalline scorodite at atmospheric pressure attracted lots of attention as it allows smelters to produce a presumably safe As-bearing residue from their waste streams, at reduced cost when compared to the autoclave processes mentioned above. There were flow-sheets already proposed in the late 1990s (Filippou and Demopoulos, 1997) and a number of processes have reached industrial scale.

Controlled seeded crystallization

The earliest approach was developed at McGill University and consists in the precipitation of scorodite by heterogeneous crystallization after the addition of seed crystals to a solution of controlled supersaturation. The pH needs to be adjusted by base addition or by warming up, which acts by adjusting pH as well (Singhania, 2000). Using lime as base leads to precipitation of gypsum together with scorodite (Fujita et al., 2008a). It has been found that Na presence in solution is detrimental to the stability of scorodite, while that of ferrous iron is beneficial (Fujita et al., 2008b; Singhania et al., 2006).

The supersaturation level needs to be controlled so that precipitation occurs in the heterogeneous precipitation regime only, otherwise the crystals would be of nanocrystalline size (instead of 6 to 10 µm) and the resulting product leaching behaviour resembles that of uncontrolled atmospheric precipitates (Demopoulos, 2009).

The seed crystals may be scorodite (preferably produced hydrothermally) recirculated back in the process, or, alternatively, they can be fine particles of other materials, like hematite or gypsum crystals. The precipitation of scorodite at atmospheric pressure at temperatures as low as 85ºC was thus considered a *"viable"* and *"robust process"*, as it produces a solid residue that can pass the TCLP test (Singhania et al., 2005).

This synthesis method has been recently industrially applied (Adelman et al., 2015). Since 2013, Codelco's subsidiary EcoMetales Ltd. (Chile) operates a plant where arsenic is leached out of copper smelter dust, oxidised (with hydrogen peroxide) and then precipitated from supersaturation conditions (pH ~ 2, T = 60 to 80º) (EcoMetales, 2014). EcoMetales does not explicitly mention the seeding material used, if any, but claim to follow the McGill process.

Simultaneous Fe(II) oxidation and precipitation

Fujita et al., (2008a) claimed that, for industrial purposes, it would be preferable to develop a seeding-free and gypsum-free alternative process. They suggested a process which uses ferrous Fe(II) ions as iron source. When oxidised with pure oxygen gas "*scorodite was readily formed and precipitated by co-precipitation of ferric and arsenic ions in an O_2 gas oxidation reaction of ferrous ion present in a mixture containing high concentration arsenic(V)"* (Equation 2).

$$4\ H_3AsO_4\ (aq) + 4\ FeSO_4\ (aq) + O_2 + 6\ H_2O \rightarrow 4\ FeAsO_4 \cdot 2\ H_2O\ (s) + 4\ H_2SO_4\ (aq) \qquad \text{Equation 2}$$

Using a redox reaction is in fact another approach to control the supersaturation level, alternative to the pH control of the previous method (Demopoulos, 2009).

Dowa Metals & Mining Co. Ltd. (Japan) seems to have applied successfully the process suggested by Fujita et al. (2008), at pilot scale, precipitating scorodite by oxidation of Fe(II) in a solution containing high As (V) concentration. The reaction starts at pH 1, and lowers down to 0.5 in the end. Without the need for heterogeneous precipitation, they claim relatively large (20 µm diameter) crystals are obtained (Fujita et al., 2012a).

The best results are obtained at 95ºC with oxygen sparging. Using air as oxidant instead of pure oxygen leads to a product with worse solubility, as does performing the precipitation at lower temperatures.

It should be noted that from a starting solution of 50 000 mg/l, Fujita et al., 2008a claim to successfully remove 97% of the As as scorodite, but this would still leave an effluent with 1.5 g/l As, much higher than the usual maximum limit values (around 0.1 mg/l), so some polishing step would be required.

Bioscorodite

González-Contreras et al. (2012) recently proposed a way of producing scorodite by biologically-assisted atmospheric precipitation. It applies the simultaneous oxidation of ferrous ions and precipitation of scorodite, as in the Dowa process, in this case with microorganisms performing the oxidation.

Crystallization still takes place at pH below 3 and temperatures above 60ºC. Extreme thermophilic archaea *Acidianus sulfidivorans* which can resist temperatures up to 85ºC

were used, because at lower temperatures moderate thermophilic microorganisms such as *Acidithiobacillus ferrooxidans* could not produce scorodite. The *Acidianus* proved resilient to As concentrations up to 3 g/l of As(V).

It is claimed that a highly crystalline product is obtained under less demanding conditions (González-Contreras et al., 2012). More specifically, González-Contreras et al. (2012) claim to produce a much larger crystal size at 150 µm instead of the 6 to 20 µm reported by the previous processes. The authors mention that their crystals are very similar to those found in nature, and that perhaps biologically assisted crystallization is the natural scorodite forming process.

The process has been studied at the pilot scale by the company Paques, which markets it as the ThioTEQ Scorodite process (Weghuis, 2013).

Hydrotermal conversion of ferric arsenate

Outotec has patented a process in which iron arsenate with Fe/As between 1 and 3.5 is precipitated first, followed by treatment at high temperature (150-200ºC) to transform it into scorodite (Outotec, 2010). Thus even though the precipitation takes place at room temperature it may be considered together with the hydrothermal methods that require more demanding conditions.

2.4 Assessing the solubility and stability of iron arsenates

The previous iron(III)-arsenic(V) precipitation processes are able to effectively remove arsenic from solutions, either at room temperature with high Fe(III) consumption (ferrihydrite/ferric arsenate), or with low Fe(III) consumption (scorodite) in autoclaves or at temperatures close to 100ºC in controlled processes. They are in fact already used for that purpose at the commercial scale in smelters worldwide.

Therefore, the main issue to be clarified regarding these precipitates is whether the solubility and long-term stability of the solid produced is in fact acceptable. It has been established that scorodite is less soluble than amorphous arsenical ferrihydrite of the same Fe/As ratio and equivalent to that of higher Fe/As precipitates (Monhemius and Swash, 1999).

Scorodite is also less soluble than several other crystalline phases studied when subjected to the TCLP test or other closed bottle leach tests, but those types of tests have been deemed not representative of actual landfill conditions (Ghosh et al., 2004; Harris, 2003; Paktunc and Bruggeman, 2010; Welham et al., 2000).

There are several reasons why. Welham et al. (2000) cover a few in their review, probably the most critical on the stability of scorodite. First of all, the fact that the standard test can be completed in less than 24 hours means long-term extrapolations should not be done lightly. That is why a number of the researchers reviewed for this text performed their tests for longer, even for months (e.g. Gomez et al., 2011). However, even though they were longer, most of them were still closed bottle tests, which is another complaint put forward by Welham et al. as it allows for reaching a chemical equilibrium that prevents further As dissolution, while landfills will have running water and no equilibrium can be reached.

Welham et. al criticise also the use of synthesised solutions, as they have no other deleterious ions that are present in real metallurgical effluents. Some later studies reviewed have used actual industrial solutions (Fujita et al., 2008a), but it is still uncommon. Another comment was that some of the very high-As metallurgical solutions will still be over the effluent limits even if 99.9% of the arsenic is removed via scorodite precipitation.

Moreover, the conditions tested by bottle tests may be misleading. In the case of scorodite, scholars put the top limit of scorodite stability at pH 7 as already mentioned during the hydrothermal precipitation chapter, observing that it releases much more As than the TCLP test limit when pH is higher than that (Adelman et al., 2015; Gomez et al., 2011; Paktunc and Bruggeman, 2010). The reason is that, as Welham et. al explain, scorodite, just as ferrihydrite/ferric arsenate, is only metastable at pH above 4, and transforms into goethite in what would be a "*potentially hazardous process*".

Welham et al. had concluded in 2000, after reviewing the state of the art on scorodite and iron arsenates that *"the only route to ensure safe, long term disposal of arsenical wastes is to investigate novel phases which possess a more stable structure towards exposure to atmospheric weathering."*

It would seem that not much has changed in this regard. A decade later, after testing the stability of their scorodite Fujita et al. (2012b) found as well that it "*appears to be important to avoid placing scorodite in a high-pH environment*". In their previous article Fujita et al. (2009), they had performed a modified 35-day TCLP test. At the end of that period they observed 3.14 mg/l in the leachate at pH 6.86 and a 351.7 mg/l at pH 9. Thus at pH just below 7 the concentration is already an order of magnitude higher than that at lower pH, and at pH 9 it was beyond what could pass the test. Their results prove the importance of pH in the disposal environment to prevent As release, and validate the complaint put forward by Welham et al.

Fujita et al. (2012b) also studied the hypothesis that the presence of iron hydroxides, such as goethite, could help stabilise scorodite. It was found that it can have some effect in the acid pH range, but it does not improve stability under alkaline conditions.

The same strong pH dependence has already been discussed with the findings by Gomez et al. (2011), who reached the same conclusion regarding scorodite disposal, advising to avoid alkaline environments.

In addition to pH dependence, scorodite "*shows decreased stability under anoxic conditions*", and when E_h decreases below 100 mV it gets decomposed (Adelman et al., 2015). Adelman et al. go on to explain that, therefore, anaerobic microbiological activity and/or unreacted sulfide minerals can decompose scorodite when they reduce Fe(III) to Fe(II). This has apparently been already observed in practice in a landfill cited in that paper.

The conclusions from all the considerations above were summarised in the guidelines proposed by Baxter and Scriba (2010):

1. Use dry storage
2. Store in a dedicated facility
3. Avoid storing scorodite with reducing agents, such as sulfides

Those guidelines, though, mean expensive requirements for arsenical waste producers and would not allow for landfilling in common landfills. Therefore, even though scorodite precipitation has gained industrial application, there is still a strong case to find an alternative that would be more robust to landfill conditions.

2.5 Alternative precipitation processes

2.5.1 Lime precipitation

Lime precipitation has been used worldwide in the past to produce calcium arsenate. Furthermore, it seems to be the procedure used by most smelters in Europe surveyed by the European IPPC Bureau (2014).

This was a recommended option (Mehta, 1981) for the production of a disposable As-bearing waste. It was later found not appropriate as it will decompose under the action of atmospheric CO_2 to form calcium carbonate (Twidwell et al., 2002, 1995). The actual stability region of the compound is thus compromised (Figure 10).

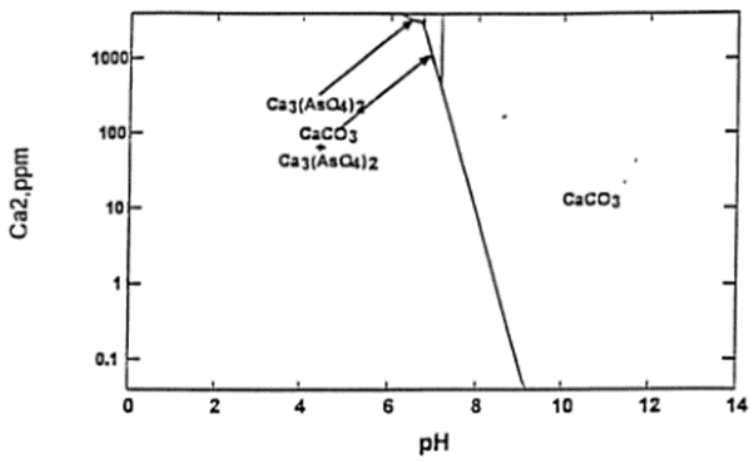


Figure 10. Stability of calcium arsenate in the presence of atmospheric CO_2. Copied from Wilson, (1998).

Besides decomposing at high pH, calcium arsenates with TCLP (i.e. at pH 5) leachate values above 950 mg/l where already observed by Swash and Monhemius in 1995. It is the very hazardous nature of this traditional process that pushed for the research of the iron arsenate alternatives in the first place.

2.5.2 Aluminium modified ferrihydrite

Single step

An improvement over the "conventional" amorphous arsenate precipitation is to add aluminium (III) to the starting solution. Hohn et al. (2006) reported better stability of the precipitates formed during laboratory tests when using molar ratios Al/As = 5 to 10 (with Al/Fe = 1).

Berre et al., (2007a) showed that the same improvement is not achieved by adding Al before hydrothermal precipitation of scorodite. The resulting mixture of scorodite and

aluminium arsenate, mansfieldite, $AlAsO_4 \cdot 2H_2O$ is more soluble than scorodite alone for any mansfieldite proportion.

Two steps

Jia et al. (2012) proposed performing precipitation in two steps. In their study, during the first step a solution of Fe/As = 2 is neutralised to pH 4 producing ferrihydrite/ferric arsenate. In the second stage, Al(III) (or Fe(III)) are deposited over the previous precipitate.

The resulting solids are of general formula $Fe_2As_1Al_2$ when adding aluminium, which gave the best results in the study. The leachability tests performed were very thorough covering pH values up to 9, and the resulting precipitate shows markedly higher stability under all conditions tested (oxic, anoxic) than a single-step ferric arsenate (of Fe/As ratio of 4). This is very relevant for waste disposal, as the two-step $Fe_2As_1Al_2$ precipitated with Ca(OH)2 showed the same leachability at pH 9 as the Fe/As = 4 showed at pH 5. That is, provided its long-term stability was better than that of iron-only compounds, this is a solid much more suitable for landfill disposal.

2.5.3 Coated scorodite

Lagno et al. (2010) researched the possibility of encapsulating scorodite with hydrate aluminium phosphate, a mineral isostructural to scorodite. This was based on the observation that a coating layer of iron hydroxide is formed when scorodite is immersed in a neutral/alkaline solution, which could be helping to reduce the dissolution rate in those conditions (Zhu and Merkel, 2001).

In a long-term leaching test under reductive conditions at pH 7, up to 6 weeks, the coated scorodite released much less arsenic than the uncoated one, the difference being of an order of magnitude, so implementation of this type of second precipitation step could prove useful. However, the case for using a "two-step scorodite precipitation" is weaker than in 2.5.2, as the scorodite process itself is already more capital intensive.

2.5.4 Schwertmannite

The mineral schwertmannite, an iron-oxyhydroxysulfate of formula: $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ has been proposed as an arsenic carrier. Arsenic adsorbs on the schwertmannite surface and it can also substitute the sulfate in the matrix up to 5.6% in mass.

It has shown short term leachability similar to that of scorodite in the study by Raghav et al. (2013). However, as the other iron-arsenic solids its long-term stability seems to be unfavourable. Schwertmannite is metastable, even though the transformation to goethite may be slowed down by As and, e.g. Si, which have a stabilizing effect. On the other hand, it is catalysed by Fe^{2+} ions.

After their long-term test, Burton and Johnston (2012) concluded that "*transformation of As(V)-coprecipitated schwertmannite to goethite causes a major increase in the extractability of solid-phase As*" and said that schwertmannite is not recommended unless "*in environments containing only modest total As concentrations*".

2.5.5 Ferrous arsenate: symplesite

The pure mineral, of formula $Fe_3(AsO_4)_2$, has a solubility product pKsp = 33.25 (Johnston and Singer, 2007), better for immobilization than that of scorodite (Annex 1). The study

by Raghav et al. (2013) validated that the short-term leaching behaviour of iron (II) arsenates is comparable to scorodite under TCLP conditions, even though it was not as good as that of schwertmannite.

The thesis by Shan (2008) reports a synthesis method, and compared symplesite to scorodite and hydroxyapatite. Symplesite can be produced at room temperature and pressure, and at a wide range of pH from solutions with Fe(II) and As(V).

Increased As release but still well below limits is observed under alkaline conditions or when reducing agents are used, so symplesite precipitates could be effective to stabilise arsenic in alkaline and anoxic waters (Drahota and Filippi, 2009; Johnston and Singer, 2007). At pH near 8 and after ageing for a year, As release remained below 2 mg/l (Daenzer, 2011; Doerfelt et al., 2015).

Welham et al. (2000) suggested the iron(II) in ferrous salts may be converted to iron(III) under the effect of atmospheric air, so they would not be suitable for disposal under oxidative conditions. This was shown by Daenzer (2011), reporting much higher release of As, up to 18 mg/l, when air is sparged on a sludge containing ferrous arsenate. This is, however, lower than the scorodite release reported in some studies when pH > 7.

The synthesis can be hindered by unwanted oxidation of Fe(II), so a nitrogen atmosphere was employed by Daenzer (2011). However, Daenzer et al. (2014) showed that low agitation speeds and covering the reactor could prevent oxidation as much as nitrogen sparging, reducing the Fe(II) oxidation to 10/15%. Daenzer (2011) also tested continuous production at laboratory scale and performed long-term leaching tests on the products. Symplesite released a maximum of 7 mg/l in closed bottle tests after 840 days, making it a quite promising option.

2.5.6 Ferric arsenite: tooeleite

This mineral with formula $Fe_6(AsO_3)_4SO_4(OH)_4 \cdot 4H_2O$) is found in nature (Nishimura and Robins, 2008) and it has been studied as a potential arsenic trap specifically for weak acid effluents from copper smelters by Opio (2013). With high arsenic content (25 wt%), Opio claims tooleite presents "*high arsenic removal efficiency, a low iron demand (Fe:As molar ratio =1.2) and precipitates easily under ambient conditions*".

It has nevertheless shown high leachability under TCLP conditions in the study by Raghav et al. (2013). Liu et al. (2015) show that *Acidithiobacillus ferrooxidans* is able to decompose tooelelite especially in the acid pH range. Furthermore, all of the tests by Opio (2013) in the alkaline pH range show high arsenic release. The only way to prevent high leaching was to calcinate the precipitate at 600ºC, even then not showing comparatively good results (13.1 mg/l for the TCLP).

2.5.7 Yukonite

Yukonite is found in some Fe/As rich settings, such as tailings ponds. If gypsum and a source of calcium such as limestone are present together with scorodite, it is possible for the scorodite to transform into the mineral yukonite, of proposed formula $Ca_2Fe_3(AsO_4)_3(OH)_4 \cdot (3+x)\ H_2O$. This is a helpful transformation that would keep some arsenic immobilised even after scorodite transforms (Bluteau et al., 2009).

Bohan (2015) concluded that yukonite is stable in the 5 to 8 pH range under oxidising conditions. Although slowly, it undergoes dissolution by reaction with CO_2 and is negatively affected by reducing conditions. Both Bohan and Gomez et al., (2010) present a synthesis procedure which starts from an As(V) solution, to which Fe(III) and Ca(II) are added to keep an 0.50/0.75/1 Ca/Fe/As ratio. The solution is then neutralised to pH 8 and aged at 95ºC for 24 hours.

Precipitates can thus be formed by room temperature neutralization (but need subsequent ageing), which actually showed lower solubility than their high temperature counterparts. The leachability of that yukonite was adequately low when no gypsum is present (<7.5 mg/l for pH 8), and much better for gypsum-saturated conditions (<0.7 mg/l).

2.5.8 Hydroxyapatite

Due to the similarities with phosphate, arsenic can form hydroxyapatite-type minerals, $Ca_{10}(PO_4)_6(OH)_2$, by substituting arsenate AsO_4 into its structure (McCloskey et al., 2005). The phosphate-free arsenate apatite end-member, johnbaumite, was synthesised by Bothe and Brown (1999) by mixing lime and arsenate solutions at Ca/As ratios from 0.8 to 4, at room temperature. Similar experiments were replicated by Zhu et al. (2006).

Precipitation with phosphate and lime has been studied by researchers at Montana Tech (Larry G Twidwell et al., 2005). It was found that phosphate-arsenate hydroxyapatite is more stable than the calcium-only arsenates when it comes to carbonation under atmospheric conditions. At P/As ratios above 5 the precipitation is actually able to remove successfully the arsenic down to low levels and produce a relatively stable compound (Miranda, 1996).

The resulting arsenated compound will be of chemical formula $Ca_{10}(As_{0.15}P_{0.85}O_4)_6(OH)_2$ for P/As = 5 and $Ca_{10}(As_{0.11}P_{0.89}O_4)_6(OH)_2$ for P/As = 7. These compounds thus present the advantage of calcium arsenate, that is, lowest solubility at alkaline pH such as that found in mature landfills, but instead show much higher resistance to carbonation. When phosphate is present, solubility did not increase significantly after 18 months of air exposure at pH 12, whereas the Ca-As compounds tested by the same authors were unstable (McCloskey et al., 2005; Saran, 1997).

Wilson (1998) removed arsenic from an initial 3.6 g/l solution by oxidation with permanganate and apatite precipitation. Excess lime is added. For example, for P/As ratios of 5, an excess lime addition of >1.75 times the stechiometric amount, helps to reduce the As concentration below the 0.4 mg/l level. Similar results are reported more recently by (Dungkaew et al., 2012).

It is also relevant that, although original procedures were performed at elevated temperatures, precipitation is achieved as well at ambient conditions (Twidwell, 2011).

Calcium-phosphate precipitation has been used at least at the pilot scale on the ASARCO smelter (US) to treat the blowdown effluent (McCloskey et al., 2005; Wilson, 1998). The operation no longer exists as the smelter was shut down in 2009, after the owner company declared bankruptcy, but the results reported showed high arsenic retention.

Shan (2008) states that this precipitation method would not be suitable when starting from high Fe solutions. In that study the leaching behaviour of high P/As (5 or 10) precipitates

had minimum release for pH 7. Within the pH 5 to 9 landfill-relevant range, the maximum is observed at pH 5 with approximately 5 mg/l. When iron is present, for P/Fe/As = 1, the release of arsenic is higher, with the maximum in that range also observed at pH 5 reaching 40 mg/l.

2.5.9 Alunite supergroup

This mineral group is subdivided in: alunite, jarosite, beudantite, crandallite and florencite. Several members of these groups have been tested for arsenic removal (Kolitsch and Pring, 2001).

Welham et al. (2000) covered the potential of jarosite as arsenic carrier and concluded that slightly acidic pH and certain sulfate(VI) content are necessary for it to be stable. Otherwise it also transforms to more stable goethite, so it would seem it is not a better option than scorodite as it produces larger volumes of waste for a similar solubility. Kendall et al., (2013) compare arsenical jarosite leaching in closed and open systems. The resulting arsenic release was completely different in each case. The study both shows that jarosite is not suitable for long-term storage of As and that leaching tests should ideally be performed in open systems with fresh solution flowing through the waste. Otherwise, leaching can be underestimated.

Viñals et al. (2010) have looked at the jarosite-like alunite phases, which have the general formula $AB_3(TO_4)_2(OH)_6$. Alunite presents Al instead of Fe^{3+} as the B so it is not reduced under anaerobic conditions, as Fe^{3+} would be. Arsenic can substitute TO_4 in the formula.

The short term stability tests performed by Sunyer i Borrell (2013) reported low solubility of arsenical alunite and natroalunite up to pH 10-11. Especially in the pH range 4 to 8, it was much lower than that of scorodite, so it is potentially much better suited for landfill disposal. Long-term tests, up to 30 weeks were also reported, in which arsenical alunites and natroalunites performed similarly to natural scorodite.

It should be noted they seem to have been closed bottle tests performed only at pH 4-5 which would not be representative of the neutral/alkaline conditions of conventional landfills. Moreover, natroalunite synthesis requires temperatures in the 180-200ºC range and is only able to carry up to 5% As to prevent too large release, making it not so attractive as an arsenic carrier.

Besides the alunite subgroup, the mineral groups crandallite and beudantite have been proposed for removing As (and other toxic metals). Islas et al. (2013) studied the best conditions to synthesise beudantite at 94ºC. On the solubility testwork performed by Krause and Ettel (1989) beudantite presented the lowest solubility, compared to scorodite, yukonite and arseniosiderite. The results from Roussel et al. (2000) also showed quite low As release at acid pH. These tests were performed only at pH around 4, though, and a major disadvantage of beudantite is a relatively low arsenic loading capability, at 10.5%.

2.5.10 Other phases

There has been a sulfide precipitation and polymerization facility in Japan (Valenzuela, 2000) and one European smelter also treats its effluents by sulfide precipitation, apparently with no specific treatment for arsenic (European IPPC Bureau, 2014). However, as mentioned before, arsenic trisulfide is soluble, especially under neutral and alkaline

conditions, and may also be oxidised under atmospheric conditions or due to bacterial activity (Riveros et al., 2001). Thus it is not considered suitable for disposal (Robins et al., 2001).

Other precipitations proposed that will not be detailed include: copper arsenate (Vircikova and Havlik, 1999), barium (II) arsenate, magnesium-bearing minerals (Opiso et al., 2010), manganese hydroxide coprecipitation (Kameda et al., 2014) and hemimorphite (Mao et al., 2010).

2.5.11 Zero valent iron

The pre-oxidation stage can be an expensive unit operation, so processes that can remove both As(III) and As(V) without pre-treatment have been studied. Zero-valent iron (Fe^0 or ZVI) has been considered one of those solutions.

ZVI spontaneously corrodes to oxides/hydroxides in solution, which form an outer layer. As(III) and As(V) soluble forms are thought to be removed by adsorption on the corrosion products and by forming complexes on the surface (Kanel et al., 2005).

Furthermore, the use of nanoparticles of ZVI (nZVI) has also been tested, as the large improvement in surface area and reactivity are beneficial for interfacial interactions. nZVI needs stabilisation, though, as the corrosion products easily build up and agglomeration occurs. Several different options have been reported, such as starch, as successful stabilisers (Liu et al., 2016).

Twidwell et al. (2004) report that reactions with arsenic are slow and have proposed that they may be improved if galvanically coupled substrates are used. They tested copper-iron couples and little improvement was observed, but they give examples of other couples that could be used.

The use of nanoparticles in general seems to have focused on *in situ* remediation. *Ex situ* applications like the ones that the smelters would require, potentially present the same problems as the adsorption and ion exchange processes, i.e. iron particles (or nanoparticles) with adsorbed arsenic still need to pass leachability and stability tests, if they are to be disposed of in landfills, and that is not clear yet. Furthermore, it is still necessary to determine the potential health or environmental impacts of nanoparticles (Karn et al., 2009).

3 Stabilisation of solids

As already mentioned, the final form of arsenic should be that of a solid compound in order to ensure it is immobilised. Some solids have already been discussed, produced after removal from solution, but it has been seen that there are doubts regarding the long-term leaching behaviour and stability of even the best options.

Shortened as S/S, the following methods consist in bonding solid waste with binders and other materials, so that a more stable product is obtained.

3.1 Cementitious solidification

The cementitious materials most commonly tested for immobilization of arsenic have been cement, fly ash and lime, and combinations thereof. Using Portland cement seems to be the most established approach, whereas adding or using exclusively fly ash or lime could lead to detrimental results (Goyal and Chauhan, 2015).

A great majority of the industrial projects analysed by the USEPA (2002) produced stabilised waste that can pass the TCLP test. Some of the USEPA tests were performed six years after deposit, and still showed little As release. However, between 9 and 19% of the landfill test leachates analysed from different industrial sites showed arsenic contents above the 5 mg/l limit and the USEPA was concerned that storage conditions were not representative of landfilled waste, so it would not be possible to reach conclusions about long-term stability.

Leist et al. (2003) performed a laboratory study on the immobilization of arsenic from mixtures containing around 10% As. They were subjected to sequential batch leaching tests. On that study the presence of calcium was found to be beneficial for As immobilization, while that of Fe was not shown to have any effect.

A pre-oxidation stage could be beneficial, as shown by Vandecasteele et al. (2002). Their waste, fly ash containing 23 to 47% As produced a leachate with 5000 mg/l of mostly As (III), so solidification with cement and lime was tested both with a pre-oxidation stage using a 30% hydrogen peroxide solution followed by stabilisation with cement and lime, and by direct solidification without preoxidation. The mixtures were in a 10:8:6:20 waste fly ash, lime, cement and water proportion.

The results from the closed bottle tests performed by Vandecasteele et al. (2002) showed, first of all, a 99.9% reduction of the arsenic release for the non-oxidised waste, from 5000 mg/l for the untreated waste down to around 5 mg/l for tests in the presence of lime, $Ca(OH)_2$, having reached a final pH above 12 during the test (German DIN standard instead of TCLP). This release is thus not representative of what may happen when subjected to the near-neutral leachates of landfills.

The oxidised waste released lower amounts of As by an order of magnitude, provided the H_2O_2 addition was large enough. Nevertheless, Vandecasteele et al. acknowledge that the pre-oxidation stage is costly and makes the processing more difficult.

The immobilization has been explained by the formation of $Ca_3(AsO_4)_2$ or $CaHAsO_3$ compounds, the latter presenting a solubility product of $Ks = 1.07 \cdot 10^{-7}$. At pH 12.5 the

equilibrium As concentration in solution for that compound on its own is thus calculated as 30.3 mg/l. However, by addition of $Ca(OH)_2$, its calcium dissolves into solution as well, reducing the equilibrium concentration through the common ion effect down to 0.47 mg/l as calculated by the authors.

This mechanism explains and corroborates the findings of Leist et al. (2003). Precipitation of low solubility calcium-arsenic compounds was also the dominant of the three ways that Dermatas et al. (2004) suggested for the immobilization of arsenic, the other being physical or chemical inclusion (via substitution into the structures of calcium silicate or aluminate hydrates) and adsorption/ ion exchange with pozzolanic products and/or clays.

On that study Dermatas et al. tested the stabilisation of both soils and artificial mixtures of clay and sand contaminated with arsenolite by perfoming semi-dynamic leaching tests. The results indicated that adding quicklime, montmorillonite clay and/or fly ash improves As immobilization. For example, untreated tailings released almost 12% of their As content, whereas a specimen with 10% lime content and another with 25% fly ash and 10% quicklime released only 0.57 and 0.15% As respectively. It should be noted that artificial mixtures showed much higher As release (over 50% when untreated) than the actual soil field samples. Following up on the previous study, Moon et al. (2010) perform the same procedure but add also sulfate. The results indicate better performance for quicklime-sulfate than for quicklime-only mortar.

As mentioned in the chemical precipitation chapter, calcium compounds suffer from carbonation, which is the transformation into calcite ($CaCO_3$) due to reaction with atmospheric CO_2 that results in remobilisation of As. By encapsulation with pozzolanic materials, it is possible to reduce this problem producing an impermeable solid monolith if it prevents the diffusion of CO_2.

The previous studies researched the stabilisation of waste (or artificial mixtures) containing arsenolite when mixed with pozzolanic materials. In a copper smelter, arsenolite can be found in the unprocessed smelter dust. However, the S/S process with pozzolanic materials could also be applied to the residuals after precipitation/coprecipitation treatments.

When iron is present, Clancy et al. (2015) report that arsenic-calcium-iron compounds will be responsible for the immobilization, instead of the As-Ca compounds mentioned above. In their study, a Portland cement, sand and water (at proportions 1:3:0.5) mortar was prepared, and mixed with 1 or 3% of iron oxide arsenic-bearing waste replacing the sand. Long-term leaching tests were performed at open containers in which mortar cubes were exposed to rainwater, being closer to closed bottle tests than dynamic ones. The volume was kept constant over 406 days by adding deionised water to replace evaporation losses and refilling with rainwater after sampling. The results showed that 0.34% of the arsenic was released from the mortar cubes at the end of the leaching test, which settled at around pH 9.

Clancy et al. showed the arsenic association with iron via μXRF analysis. Short term tests were also performed, that showed arsenic release greatly increased for pH below 4. The authors thus state that disposal of cement stabilised arsenic and iron-bearing waste could be safe provided acid pH is avoided. Given the typical landfill conditions, acidic conditions below pH 5 are not expected, so it should be achievable.

Miller et al., 2000b tested the immobilization of soil contaminated with arsenic both with cement only and with cement and additives such as iron salts. Ferrous salts showed the best performance so their addition was recommended. In that study, the authors also compared the leachability (according to the TCLP test and the ANS semi dynamic test) based on curing time, observing certain amount of improvement as hydration progresses.

An important issue associated with cement stabilisation is the "bulking" of the waste. When using cementitious materials there is a huge increase in the waste mass and volume due to the proportions in which the substances are mixed, and especially when compared to the arsenic-loading capability of chemical precipitates from the previous chapter (Goyal and Chauhan, 2015).

Overall, the research shows that cement stabilisation can lead to low solubility solids, although many of the tests reported were short-term and might not be representative of landfill conditions, as was the case for chemical precipitates. Moreover, the proportions of raw materials in the mixture should be studied case by case based on the original waste composition. The costs according to the (USEPA, 2002) ranged from $60 to $290 per short ton. Updated for inflation and adjusting for units and exchange rate, that would translate into 78 to 378€ per metric ton in 2016, and the process is usually considered cheap.

3.2 Other materials

One unsuccessful attempt to encapsulate in silicate gel has been recently reported by Adelman et al. (2015), which actually showed an increase in arsenic release.

Shaw et al. (2008) tried to solve the problem of As-loaded sorbent materials by encapsulating them within polymeric matrices. The matrix was made of polystyrene butadiene and epoxy resin. The new matrix showed a much greater arsenic retention capability than that of a cement matrix. Once more, the problem with the research, acknowledged in the article, is the need to study the long-term stability under landfill conditions of the resulting material.

3.3 Vitrification

Embedding waste in a glass matrix is an approach used, for example, for managing radioactive waste. It is also reported for various types of other waste: electric furnace dust (Pelino et al., 2002), fly ash and bottom ash from municipal solid waste (Park and Heo, 2002; Xiao et al., 2008) or jarosite precipitates from Zn hydrometallurgy (Pelino, 2000). Vitrification was deemed the BDAT by the USEPA in 1990 (Rosengrant and Fargo, 1990) for As-containing solid waste. The goal is to make arsenic chemically part of a glass matrix. This is achieved by applying heat to the waste mixed with glass-forming compounds. Chemical changes occur e.g. converting arsenates to silicoarsenates, which fix arsenic into a leach resistant mass.

High temperatures are required, from 1000 to 1600ºC, which will result in arsenic volatilization as in the case of smelters. Any dust and solids produced after condensation need to be collected and treated separately or recirculated. Alternatively, pre-treatment of the waste to form non-volatile compounds which can more safely be vitrified has been

applied. One method consists on roasting a mixture of lime and As-bearing waste so that less volatile calcium arsenate is formed (USEPA, 2002).

The USEPA (2002) reports up to 99.99% reductions in leachability from high-As industrial wastes. The maximum amount that can be removed by traditional vitrification is limited by, among others, the solubility of arsenic in the glass matrix, restricted to the 1-3% range according to the USEPA. Deleterious compounds for the immobilization of As include chlorides, fluorides, sulfides and sulfates, whereas sand and slag-forming materials are beneficial.

Lemieux et al. (2013) have recently revisited the application of the process for As immobilization, as part of the company Dundee Sustainable Technologies. They claim that their vitrification process results in a product with better long-term stability and lower volume than scorodite, and that energy costs are comparable to the scorodite precipitation reagent costs.

One of their major claims is that glass with up to 20% As content can be produced, much higher than in the USEPA report. The process consists in the simultaneous oxidation of arsenic trioxide (As_2O_3) to arsenic pentoxide (As_2O_5) and formation of calcium arsenate with calcium hydroxide, $Ca(OH_2)$. The resulting $Ca_3(AsO_4)_2$ is stable under temperatures as high as 1455ºC and can be used for glass forming without high volatilization losses.

Another claim is that "cheap" reactants can be used: manganese dioxide from pyrolusite (MnO_2) as oxidant and recycled glass to provide glass forming elements (Dundee, 2013). MnO_2 allows for the oxidation of arsenic trioxide when mixed as a slurry, and is later on incorporated into the glass structure with ease. Equation 3 shows the reaction that describes the process.

$$As_2O_3 + 3\ Ca(OH)_2 + 2\ MnO_2 \rightarrow Ca_3(AsO_4)_2 + 3H_2O + 2\ MnO \qquad \text{Equation 3}$$

The testwork cited in their patent (Lalancette et al., 2015) was performed with pure arsenolite, but it is claimed that impurities are not detrimental as long as the ratio of main glass components is maintained (Table 5). Care should be taken to avoid excess SiO_2, as it could lead to substitution of As_2O_5 and its vaporization.

A flow sheet proposed for the treatment of flue dust with As contents around 30% is shown in Figure 11. By water leaching at 100ºC, 75 to 80% of the arsenic is removed and then mixed with lime and manganese oxide to form the calcium arsenate. Recycled glass is then added to the mixture which, after drying, goes into the melting stage to produce the As-bearing glass. Lemieux et al. (2013) explain that the residual solid containing the non-leached As could be vitrified as well.

At the beginning of 2016, Dundee had already performed pilot work and signed an agreement with a gold company to determine the feasibility of integrating their process to the existing operation (Marketwired, 2016). Even more recently, there has been an agreement between EcoMetales and Dundee Sustainable Technologies that aims to "*stabilize arsenic using vitrification technology as a complement to EcoMetales Technology (scorodite)*" (Dundee Sustainable Technologies, 2016).

Table 5. Composition limits for the vitrified glass.

Mass %	SiO_2	CaO	As_2O_3	As	MnO	Na_2O	Al_2O_3
min	50	5	1	0.4	1	8	0
max	75	15	20	7.6	15	14	3

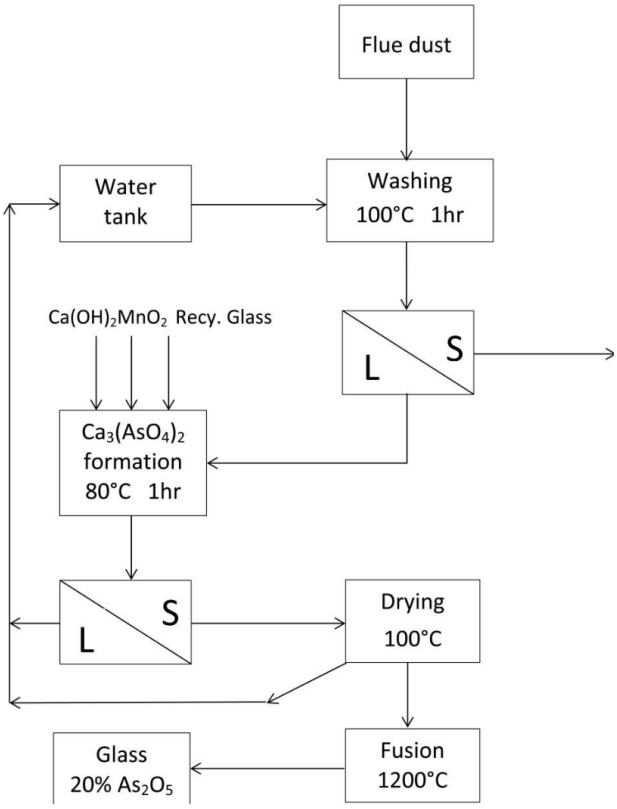


Figure 11. Vitrification process flowsheet, extracted from Lemieux et al. (2013).

The main obstacle for vitrification processes is their cost. The USEPA (2002) reported costs from $375 to $475 per short ton (489 to 619€ per tonne in 2016) and the European IPPC Bureau (2006) report on Waste Treatment Technologies states costs from 112 to 560€ per tonne, thus the upper limit seems much higher than that of cementitious solidification. High costs may have been calculated considering materials other than the ones proposed by Dundee.

3.4 Incorporation into products

Even though arsenic on its own has not much market demand, it could potentially be incorporated into products without being detrimental. Bricks incorporating arsenic have been discussed by Hassan et al., (2014) and Sullivan et al., (2010). It could also be that some glass products could be cast from vitrified waste, provided they were safe enough. This would be an ideal solution from the resource efficiency point of view. In any case, those bricks should also be another variant of a stable and insoluble solid, especially if they are going to be placed next to people. Given the understandably bad reputation of arsenic, it seems unlikely people will gladly use As-containing products, so maybe some specific industrial niche use should be identified where there could be fewer concerns.

4 Conclusions from the literature survey

The review of the literature stressed the need for a long-term solution to the arsenic problem in the metallurgical industry. The ferrihydrite/ferric arsenate precipitates are considered unsafe in the long term because they convert to more stable minerals releasing arsenic in the process, producing waste that would need monitored (and expensive) storage. Other precipitates used in the industry, such as calcium arsenates produced by lime precipitation, are considered unsafe as well.

A few thoroughly researched areas, like adsorption, may easily remove arsenic from a few mg/l down to µg/l, as required for drinking water standards. Their proponents do not often explain how exactly the rejected concentrated solutions or solids could be safely managed. In the case of nanoparticles, there is still not enough evidence that releasing them into the environment will be harmless in the long term. In any case, they are not so suitable for the treatment of metallurgical effluents containing several g/l of arsenic.

A few alternative options have been applied up to commercial or pilot scale specifically for the removal of As from metallurgical effluents. Processes by EcoMetales, Dowa Metals and others claim to produce safe scorodite waste under atmospheric conditions and, thus, at relatively low cost. The review of the literature points out, though, that scorodite needs oxidising and near neutral conditions to prevent solubilisation, and could present problems when placed in common landfills as they mature and reach more alkaline conditions.

Other promising methods have been identified that could be at least as effective as scorodite, such as two-step precipitation methods and alternative phases like symplesite. In both cases, the technology itself is not far from existing practice, so their implementation industrially does not present huge challenges.

If solids produced by the previous or other methods are still not stable enough, there are methods to stabilise them. Mixing with cementitious materials may be able to generate a safe monolith, but a large volume of waste is produced as a result. Quite recently, the Dundee Sustainable Technologies vitrification process claims to produce waste safer than scorodite precipitates and to do so economically.

One issue that has arisen from the literature review regardless of the method is the problem of testing As mobility adequately. If arsenical waste producers want to reduce costs by producing a non-hazardous waste that can be stored in normal landfills, then testing should be representative of the actual conditions of those landfills and the changes that are known to occur in them, for example the pH increase up to 9 shown by mature landfill leachates.

Bottle leaching tests such as the TCLP, and variations of it, show the short-term behaviour of waste under certain conditions. Due to their simplicity, they are the tests most often reported in the literature, but have been found lacking in a number of ways. At the very least, bottle tests should be done at several pH values that are relevant for the disposal conditions.

Lastly, actual metallurgical solutions and solids should be used, instead of artificially prepared ones in the laboratory. This way all deleterious and beneficial ions can be taken into account, as it has been found that the stability of precipitates can be modified that way.

4.1 Selection of methods to be tested

The raw material for testwork was solid waste produced after neutralization of smelter effluents. The options that could be studied directly on this solid waste would thus be amongst those from Chapter 3.

The methods that seem more robust for stabilisation are cementitious solidification and vitrification, and successful applications have been found. Cementitious solidification of the waste is already being studied by the company, so it was not considered for this work. Therefore, the only solid stabilisation technique studied was vitrification.

The methods from Chapter 2 were all precipitation methods starting from solutions. In order to test alternative precipitation methods, the procedure will start by dissolving the neutralization cake to produce an effluent similar enough to the ones smelters may typically produce. Besides, as many of the literature tests are performed on synthetic solutions prepared from pure reagents, using an actual "metallurgical" solution provides more useful information for practical purposes.

Precipitation methods abound as seen in Chapter 2, so only a small number could be tested. The selection focused on those that have been researched more thoroughly, from continuous bench scale tests up to the industrial scale. Synthesis conditions have been considered, discarding methods with higher temperature requirements, for example.

The selection of methods is described in Table 6, and a few examples of the reasons why some precipitates were not considered any further.

Table 6. Selected and discarded methods for the testwork.

Chosen precipitates and label used	Section	Largest scale	Advantages	Disadvantages
Fe8As (ferrihydrite)	2.3.1	Industrial	Proven technology, BAT according to USEPA Low temperature process	Long-term transformation with As release High iron consumption for low solubility
Al2Fe2As	2.5.2	Bench (Noranda Horne smelter 2-step but with Fe-Fe)	Easily implemented Much lower As release than Fe8As Low temperature process	Long-term transformation with As release (?)
Scorodite by controlled seeding	2.3.3	Industrial (Ecometales/Codelco)	High theoretical arsenic loading Lower iron consumption than previous methods	Temperature from 70 to 100ºC required Potentially too high leaching at pH above 8 Long-term transformation with As release
Symplesite	2.5.5	Continuous bench scale	Low temperature process High arsenic loading	Potential instability under oxidising conditions
AHAP (As-hydroxyapatite)	2.5.8	Pilot plant on real effluent	Low temperature process	Low arsenic loading Hindered by iron in solution

Discarded		Reasons for not continuing
Yukonite	2.5.7	Relatively more complex synthesis, including ageing at 95ºC. Tested only for laboratory solutions.
Schwertmannite	2.5.4	Relatively more complex synthesis, includes dialysis, temperatures up to 60ºC.
Natroalunite group	2.5.9	Relatively more complex synthesis, at high temperature and pressure.
Others		No other precipitate shows clear stability advantages and their applicability to industrial effluents is unknown.

5 Research methods

5.1 Summary of the testwork

A graphical summary of the testwork performed is shown in Figure 12. The raw material has been stabilised by vitrification, trying 3 different formulations. Five alternative precipitation methods have been tested on the solution resulting from leaching the original solid. For each of the solids produced, the number of leaching tests is as shown in that figure, trying to reach different final pH conditions from the landfill-relevant range.

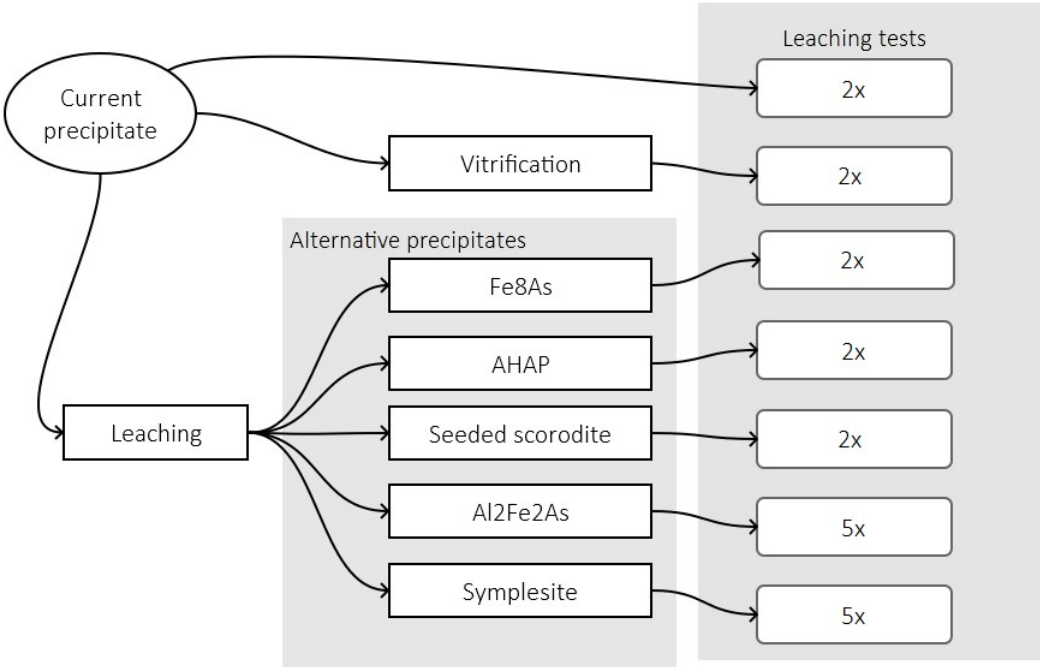


Figure 12. Summary of the testwork performed.

5.2 Test materials

Waste from a copper smelter treatment facility was used as raw material for the testwork. It is called the "neutralization cake" as it is the filtered product resulting from neutralization (with lime) of weak acid and spent electrolyte. It is a fine solid with median size between 20 and 30 µm.

The material is the same as in the study by Sunyer i Borrell (2013), which had characterised it showing the major elements are calcium and arsenic. (Table 7).

Table 7. Major elements of the neutralization cake, as previously determined by Sunyer i Borrell (2013)

Ca	22.80
As	5.23
Ni	2.65
Fe	1.08

Table 8. Mineralogical composition according to the company.

Crystalline fraction determined by XRD	$CaSO_4 \cdot 2H_2O$	40.4
	$CaCO_3$	8.2
Amorphous fraction (total 51.4%)	$Ca_3(AsO_4)_2$	38.0
	$FeCO_3$	7.0

A different characterization study by the company included mineralogical composition (Table 8) and thermogravimetric methods. They showed evaporation of water, calcination of siderite, and decomposition of dehydrated calcium sulfate, but did not report any As_2O_3 vaporization. The weight loss after heating to 1000ºC was 25%. Arsenic was described mostly as part of Ca-As compounds such as calcium arsenate, and also as Ca-Fe-As compounds, after SEM-EDS analysis.

5.3 Sample preparation

The company submitted 24 samples in bags, which had been taken over a 2-month period. There was in total of 59.08 kg of sample, split in 18 neutralization cake samples and 4 samples of "*sodium sulfate cake*". The sulfate cake and the neutralization cake were to be mixed in the proportions 0.09 to 1 respectively. The reason is that the sulfate cake is the result of a processing route that is not always in operation, but was at the moment of collecting the samples.

The water content was determined by drying samples of the cake at 105ºC. Next, the whole mass of the filter cake was dried at 60ºC. Once dried, it was possible to mix and homogenise it. It was necessary to break up big particles of cemented material before homogenization was possible, as seen in Figure 13.

5.4 Composition of the cake

Ever since the original waste had been mixed with the sodium sulfate cake, and in order to verify that the samples corresponded to a good degree to the previous description, their composition was determined.

After mixing and homogenising with the sodium sulfate cake, samples were taken to perform a 4-acid digestion followed by analysis by ICP-OES. For the digestion, a sample of around 0.5 g (weighted to 0.1 mg) is digested with 10 ml aqua regia and 4 ml hydrofluoric acid, heated for 2 hours at 100ºC, 2 g boric acid added, agitated and left for 15 minutes. It is filtered through a membrane filter prior to analysis in the ICP-OES equipment shown in Figure 20.

5.5 Vitrification

An initial attempt at vitrification of the waste tried to follow the method patented by Lalancette et al. (2015). Arsenic in the waste is already mostly present as calcium arsenate, so it was hypothesised that there would be no need to add extra calcium or any oxidant.

A clear glass container was used as the source of glass forming material. It was thoroughly cleaned and then finely ground in a ring mill. The typical container glass composition was assumed: 75% SiO_2, 15% Na_2O and 9% CaO (Worrell and Reuter, 2014). In order to keep the silica content of the final vitrified product at 50% and as the cake does not contain SiO_2, the maximum waste loading is 33%.

After weighing 5.1 g of the filter cake and 10.2 g of ground glass, they were mixed in an alumina crucible. The crucible was placed in an oven with a maximum working temperature of 1250ºC. This temperature is enough according to the patent by Lalancette et al. The heating and cooling rates were controlled to avoid breaking the crucible, so the maximum temperature was reached after 4 to 5 hours, instead of 1 hour in the patented method.

Once the maximum temperature was reached, it was maintained for 20 minutes and then the crucible removed to pour the melt into a steel plate for quenching. However, this first attempt failed at melting the solids. Not being able to pour the product out of the crucible and to avoid breaking the crucible, it was placed back into the oven, for slow cooling. Without quenching, it was clearly visible that crystallisation had taken place and the product could not be considered a glass.

Another composition that could more easily melt under 1200ºC was tested by using sodium carbonate (Na_2CO_3) as flux. This is a departure from the patent, which claims no additions other than ground glass, manganese oxide and calcium oxide are used when vitrifying at temperatures 1100-1200ºC.

First, 9 g of Na_2CO_3 were added to the first crucible containing the crystalline product. A new mixture of 1.70 g of cake, 15.02 g of glass and 6.20 g of Na_2CO_3 was added to a second crucible. Both crucibles were heated up to 1200ºC in a period of 4.5 hours with stabilisation for 20 minutes and in both the solids had melted. Each melt was subsequently poured onto a steel tray to quench. Crucibles were allowed to cool faster than before as well (luckily not producing any damage) and the product that remained inside (a high proportion) was visibly glassy as well at least in the case of the new mixture. Thus the two masses of the new mixture were put together so as to produce enough sample mass for further testwork.

In order to verify that As had not volatilised, an 0.5 g sample of the vitrified product was ground and subjected to 4-acid digestion and analysed with ICP-OES, and so was another 0.5 g sample of the cake originally used for vitrification, following the steps described in section 5.4.

5.6 Leaching to produce an As-bearing solution

The leaching testwork followed the ones described by Sunyer i Borrell (2013) and Smetanin et al. (2007). Smetanin et al. successfully leached most arsenic out of the filter

cake from a smelter with similar composition (50% gypsum, 5 to 10% arsenic). The requirements they found to be optimal are shown in Table 9. Up to 92.5% As extraction can be expected with sulfuric acid under those conditions. It should also remove Zn, Sb and 70% of the Sn, which are minority compounds in the cake.

Table 9. Leaching of arsenic from filter cake with sulfuric acid.

Optimal	17.3% H_2SO_4 solution (with density 1.12 kg/l)	
	0.32 kg H_2SO_4 / kg cake	1.96 L acid solution / kg cake
	T = 20 º C	
	2 steps of 10 minutes	

Preliminary sulfuric acid digestion testwork was performed on 1 g samples, A and B, leached respectively with 4 ml and 8 ml of 1 M sulfuric acid, and subsequently brought to 100 ml. Sample C was 4-acid digested (as in section 5.4) and total extraction of As and Fe was assumed for those conditions. The samples were then filtered and the filtrate analysed by ICP-OES, with results as shown in Table 10.

Table 10. Preliminary digestion results.

Sample	A		B		C
Soluble with:	0.38 g H2SO4/ g cake		0.76 g H2SO4/ g cake		4 acid
	wt.%	% extrac.	wt.%	% extrac.	wt.%
As (%)	4.4	62.9	5.9	84.3	7
Fe (%)	0.1	6.8	1.3	72.1	1.8

The resulting solution concentrations from the preliminary testwork proved too low (less than 0.5 g/l) so the actual digestion was performed with more concentrated acid solutions, more similar to those reported by Smetanin and Sunyer.

Two dried and homogenised 250 g samples were digested with one liter sulfuric acid and then filtered with Whatman Grade 42 filter paper. Sulfuric acid with a 1.55 M (approximately 15 wt%) concentration was used as leaching agent. The volume of acid solution used was that to produce a ratio of 600 g H_2SO_4 / kg of cake. According to preliminary digestions, this should result in around 75% As extraction and produce a 10 g/l solution.

After leaching for one hour, the first batch of digestions could not be filtered until the following day. Samples of the filtrate were taken and submitted to ICP-OES analysis in a Varian machine.

5.7 Oxidation of arsenic (III)

The solution was oxidised as all the precipitation methods tested start from As(V) solutions. In her study, Sunyer i Borrell (2013) had determined As(III) amounted to 50% of arsenic in solution. The discussion in section 2.1 showed that potassium permanganate $KMnO_4$ is an effective and cheap oxidant, and it was used in this study.

At first, enough of a 5% permanganate solution was prepared to result in 4 times what would be required to oxidise As(III). A preliminary oxidation showed that the colour change induced by permanganate ions in solution was clear enough to be used for a

determination of oxidant consumption by titration. Therefore, the amount of permanganate used for the following tests was determined as 1.35 g $KMnO_4$ per 100 ml of the starting solution.

5.8 Precipitation testwork

5.8.1 Ferrihydrite/Ferric arsenate precipitation

The procedures described by several authors were reviewed and synthesised to try to produce stable solids (Jia et al., 2012; Krause and Ettel, 1989; Raghav et al., 2013).

First, 50 ml of the As-bearing solution were oxidised. Next, an Fe(III) solution was prepared by dissolving 20.15 g of $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$ in 84 ml of water. After mixing this iron solution with the As solution, the resulting mixture has an Fe/As ratio above 8 (Figure 17).

Milk of lime with a 1 M concentration was prepared by adding water to 10.04 g of $Ca(OH)_2$ up to 135 ml, keeping it suspended by stirring. The lime slurry was then added relatively quickly with a graduated pipette until pH 4 was reached, in less than 10 minutes. The precipitation was observed in the process, which required 80 ml of the 1 M lime solution.

After reaching the target pH, stirring was stopped and the slurry filtered. The solids were allowed to dry in air and not in the oven to prevent thermal conversion of ferrihydrite into Fe-hydroxides, for 48 hours. The clear filtrate (Figure 18) was stored for analysis. All the steps were performed at room temperature, approximately 27ºC.

5.8.2 Two-step aluminium and iron precipitation

The procedure after oxidation was basically the one described by Jia et al. (2012). 200 ml of As-bearing solution were oxidised with permanganate. For the iron solution 20.57 g of $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$ were dissolved in 86 ml of water and as aluminium source 20.26 g of $KAl(SO_4)2 \cdot 12\ H_2O$ were dissolved in 194 ml of water.

As shown in Figure 19, 47.60 g of $Ca(OH)_2$ were stirred in 640 ml of water. The Fe-solution was mixed with the As-solution, producing a molar Fe/As ratio above 2. Lime was added with a pipette to raise the pH, first above 4. After the first addition, pH reached 4.57 and the solution was left for 1 hour at that pH.

The Al-solution was added then and the pH raised with more lime addition, until at least pH 8, in fact reaching a final value of 8.85. The total lime addition for both steps was 260 ml.

Stirring was stopped, the slurry was filtered and the liquid stored for further analysis. The solids (Figure 21) were re-washed with demineralised water after the filtration and air-dried for 48 hours. The whole procedure was performed at room temperature, approximately 27ºC.

5.8.3 Gypsum-seeded scorodite precipitation

There are multiple ways to precipitate scorodite, as discussed in section 2.3. The option studied was that of seeded crystallization. The procedure followed mostly the one described by Singhania et al. (2005), who proved that seed different from scorodite can be

successful. No hydrothermal or natural scorodite is needed, and gypsum can be used instead if in sufficient concentration and with enough reaction time, i.e., above 80 g/l and for more than 2 hours.

The procedure (Figure 22) started by oxidising 500 ml of As-bearing solution. Then, 15.80 g of $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$ were dissolved in 67 ml of water. Both solutions were mixed resulting in a molar ratio Fe/As = 1, and the beaker was placed in a "water bath" built by placing a larger beaker on top of a magnetic stirrer with a heater. The larger beaker was filled with water and the heating plate was turned on. The beaker with the solution was placed inside and stirred constantly.

As the temperature rose, a cloud of precipitate was observed, which is also described by Leetmaa (2009). The goal was to reach more than 90ºC, but the water bath that was set up showed limitations, and the temperature stabilised only at 80-82ºC.

After the temperature was stabilised, the non-scorodite precipitate was redissolved by adding 350 ml of 1 M sulfuric acid. Next, 113.29 g of gypsum powder were added to act as seed, resulting in a concentration above 100 g/l.

The beaker was kept stirred and at 82ºC for 5 hours after seed addition. The effect of the precipitation was observed as the solution, which had returned to the original green colour after re-dissolution, started to take on a blue colour. The resulting slurry was then allowed to cool and filtered. The liquid was stored and the solids were re-washed and then oven dried at 45ºC.

5.8.4 Symplesite precipitation

Ferrous arsenate synthesis followed the batch procedure described in Daenzer et al. (2014). In that study the authors showed that lowering the stirring speed and covering the reactor was as effective as N_2 sparging to prevent oxidation of Fe(II), so those guidelines were followed.

The procedure (Figure 23) was performed starting from 200 ml of oxidised arsenic-containing solution. 23.73 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 158 ml of water, and then added to the As solution, which was subsequently covered.

While maintaining a low stirring rate below 500 rpm, milk of lime (made by mixing 20.58 g of $Ca(OH)_2$ in 500 ml of water) was added to increase the pH. 400 ml of the base were necessary to reach a final pH of 8.5.

Once the target pH was reached, the slurry was filtered. The solids (Figure 21) were re-washed and oven dried at 45ºC. Both the filtrate liquid and the washing liquid were stored for analysis.

5.8.5 Arsenate hydroxyapatite precipitation

It was performed following the procedure described by researchers at Montana Tech (for example, Miranda, 1996).

As before, 200 ml of As-bearing solution were oxidised. Then 10 ml of 85% phosphoric acid were dissolved in 200 ml of water. A first batch of lime was prepared, enough to reach the Ca/(P+As) molar ratio of 1.67 by adding 21.19 g of $Ca(OH)_2$ to 285 ml of water. In

case that amount was not enough to reach the target pH, another 31.76 g of calcium hydroxide were dissolved in 427 ml of water.

The phosphoric acid solution was added to the As-bearing solution, which was kept stirred constantly and heated up to 30ºC with a hot plate (Figure 24). The stoichiometric amount of lime was added and the pH reached only 4.79. More lime was added so as to reach the target pH range of 11.5-12.5. 125 ml of the previously prepared milk of lime were necessary to reach a final pH above 11.5. After lime addition the reaction was continued for 2 hours. No more lime was added as the pH remained constant at an average of 11.99. The temperature was kept at 30ºC.

After 2 hours the slurry was filtered. The solids were re-washed before being oven dried at 45ºC and the liquids (filtrate and washing liquid) stored for later analysis.

5.9 Batch leaching tests

5.9.1 Natural pH (based on EN 12457-4)

The test procedure tried to imitate the conditions described by the European standards EN 12457-4 and 14429. The target dry sample mass was 15 g as in EN 14429, but this was not possible for all solids, and the lixiviant addition was such that a liquid/solid ratio of 10 was achieved.

The lixiviant addition takes into account any water already present in the solids, so their water content was first determined by drying small samples of approximately 1 g at 105ºC for 24 hours.

A shaking table was used as agitator, and the leaching bottles placed horizontally to induce a motion similar to rolling at relatively mild speed (trying to imitate a 10 rpm rolling motion as in the standard, Figure 25). The tests lasted 24 hours as in EN 12457-4.

5.9.2 With initial acid/base additions (based on EN 14429)

The previous tests are similar to those used for screening/compliance in the EU. Some of the solids, however, equilibrated at pH values that are quite far from the typical range that can be found in landfills of any type.

Based on the natural pH determined previously, a new "target" pH was set, that would help to define the behaviour in the landfill-relevant 5 to 9 pH range. The acid/base amounts prepared were based on the typical values reported in EN 14429 for acid/base consumption of some waste types. Up to 4 mol of H^+ or OH^- were prepared per kg of sample, depending on whether the natural pH was acid or alkaline and the target pH for the test. The lixiviant was added then in several steps over a period of 4 hours, adjusting acid/base when necessary.

This approach did not allow to reach the target pH in all cases, as the acid/base consumption was not properly known beforehand and it proved to be unexpectedly high or low in some cases. The lixiviant (and acid/base) additions for each test are shown in Annex 3.

For quality control, two blank tests were also performed, in which water and water acidified to pH 6 was subjected to the whole procedure. Two of the solids were tested in

duplicate, so as to get an estimate of the standard deviation and replicability. Not all tests could be performed in duplicate due to sample mass available, as well as time constraints and other practical issues.

5.10 Analysis

Elemental determination was performed with a Varian (now Agilent) ICP-OES system with radial detection.

Figure 13. Different stages of the sample preparation: (a) as-received filter cake, (b) after drying, (c) breaking up the large solidified particles so that homogenization is possible and (d) homogenised samples of the neutralization and sulfate cakes, before mixing.

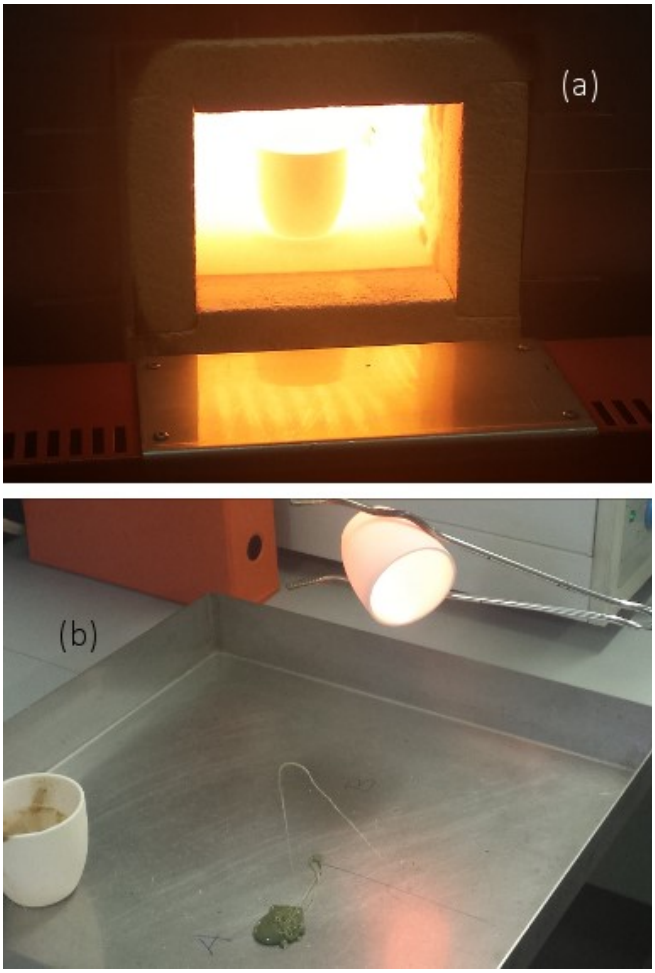


Figure 14. (a) Alumina crucible inside the oven at 1200ºC. (b) Pouring the contents of the crucible onto a steel plate for quenching.

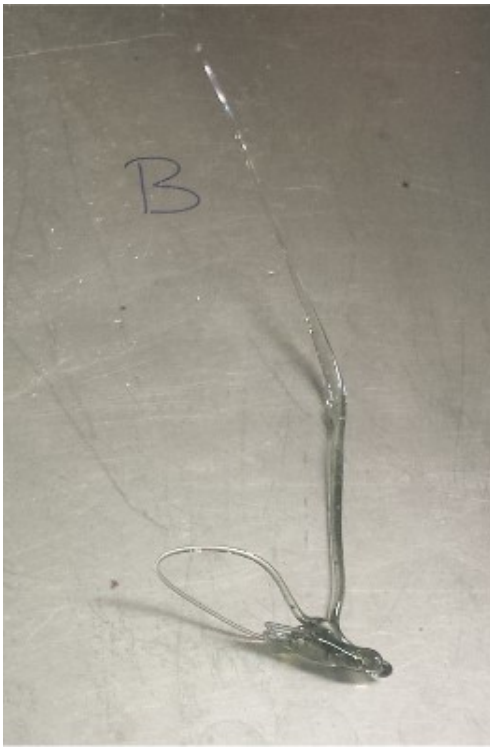


Figure 15. Product of the vitrification at 1200ºC with Na_2CO_3 added as flux.

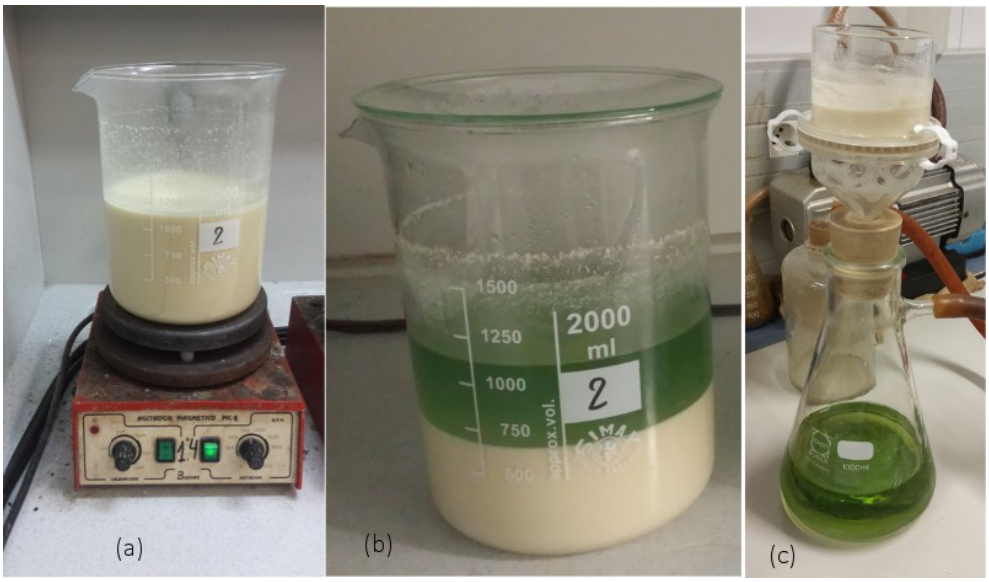


Figure 16. Pictures from the digestion procedure: (a) stirred leaching over one hour, (b) solid-liquid separation observable after a short time (c) separating the As-bearing solution (green) from the leach residue.

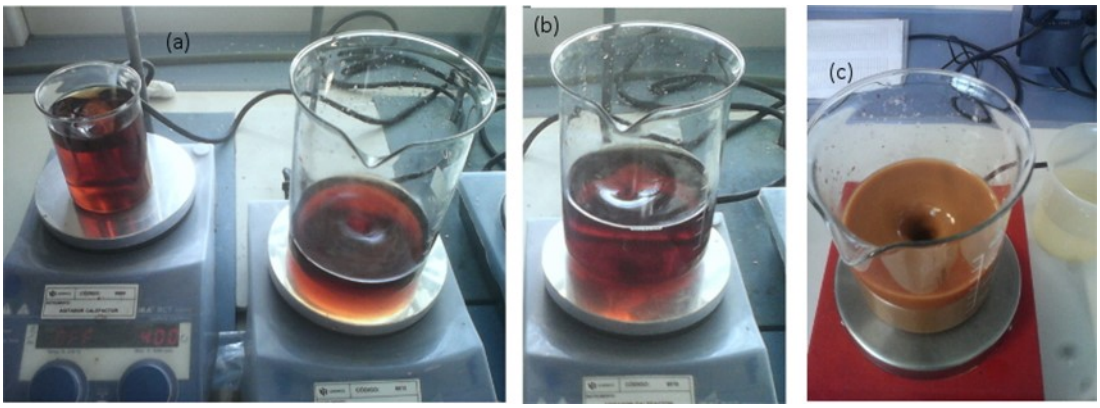


Figure 17. Ferrihydrite precipitation: (a) oxidised starting solution (right) before mixing with the iron solution (left), (b) mixed Fe/As = 8 solution, (c) after adding base the precipitate forms.

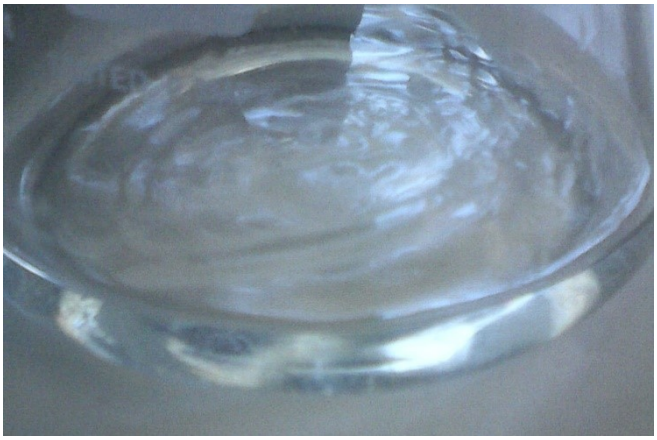


Figure 18. The filtrate is a clear solution, indicating that the process has successfully removed most of the dissolved metals from the original solution (of brown/red colour after oxidation).

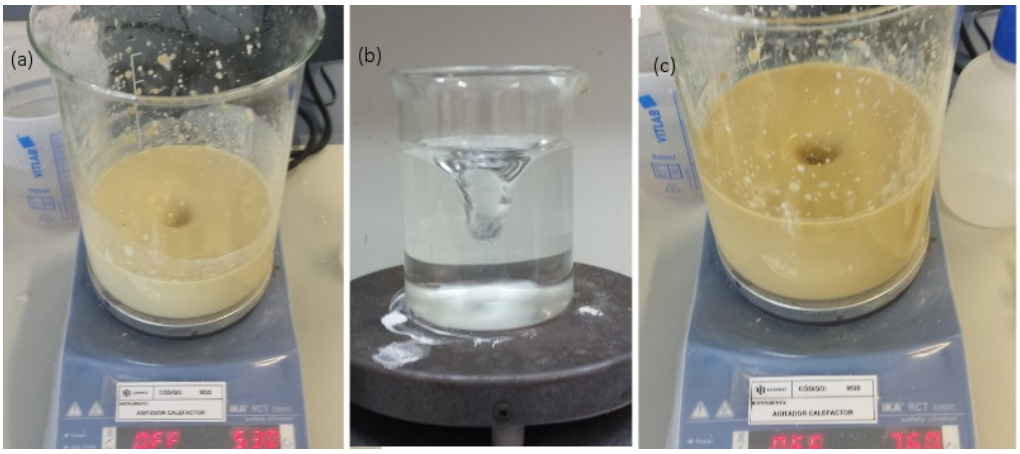


Figure 19. Two-step Al/Fe precipitation process: (a) 1st step, increasing pH to 4 by lime addition to the Fe/As solution, (b) aluminium (III) solution, (c) 2nd step, increasing pH to 8 after adding the aluminium solution.

Figure 20. ICP-OES instrument used for elemental determinations.

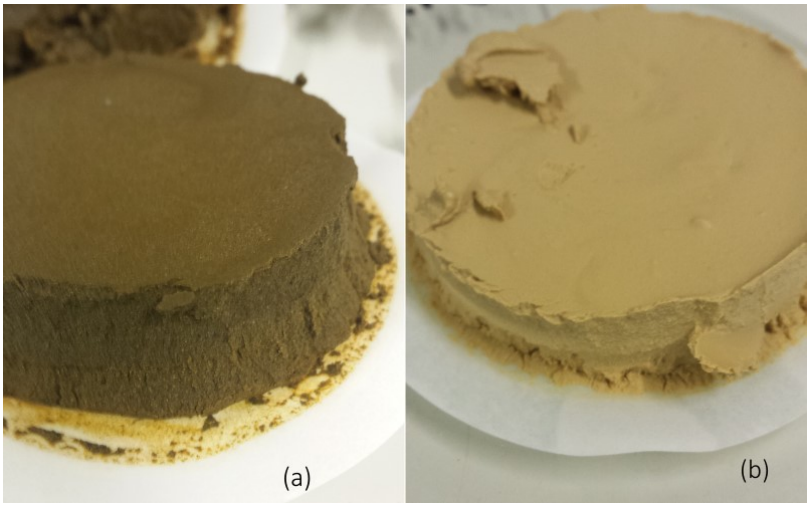


Figure 21. Solids produced after (a) symplesite precipitation and (b) Al2Fe2As precipitation.

Figure 22. The scorodite precipitation procedure: (a) set up after oxidation, (b) precipitate forms upon temperature rise, (c) after dissolving with acid the precipitate formed, (d) after gypsum seed addition, (e) the green colour is noticeably fading away mid-precipitation, (f) the solution after 5 hours.

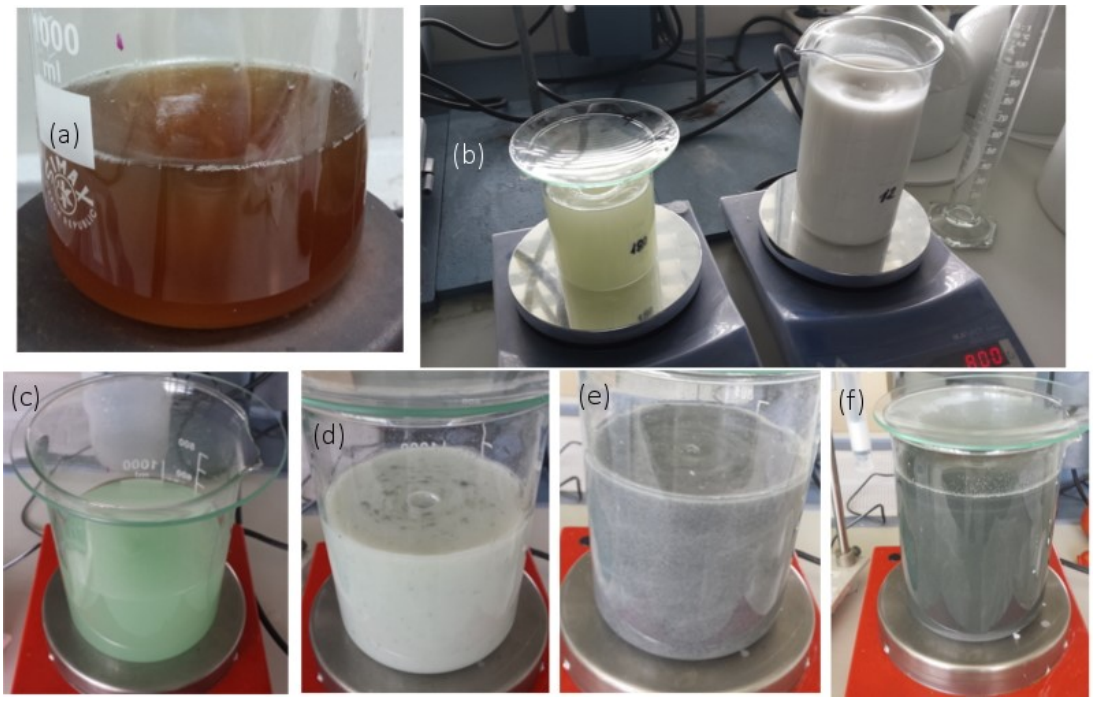


Figure 23. Symplesite precipitation process. By mixing the (a) oxidised solution with the (b, left) iron (II) solution, the solution in (c) is obtained. Milk of lime (b, right) raises the pH to 12 and leads to the production of a black precipitate (d to f). Beakers were covered to prevent Fe(II) oxidation.

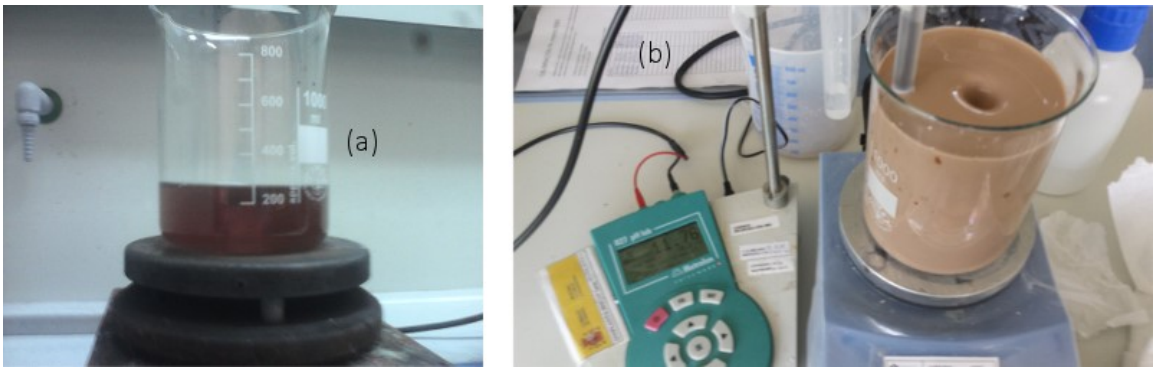


Figure 24. (a) AHAP initial solution after oxidation and phosphoric acid addition. (b) Stabilization at pH 11.5-12.5 after lime addition.

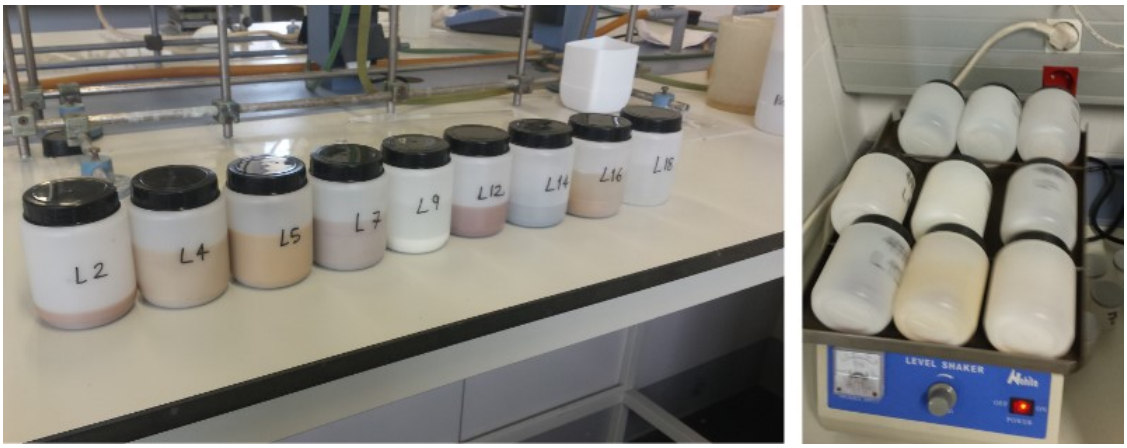


Figure 25. Leaching bottles after preparation and during the test under agitation.

6 Results and discussion

6.1 Characterization of the cake

The proportion of major elements of the cake, as determined by 4-acid digestion and ICP-OES analysis is shown in Figure 26.

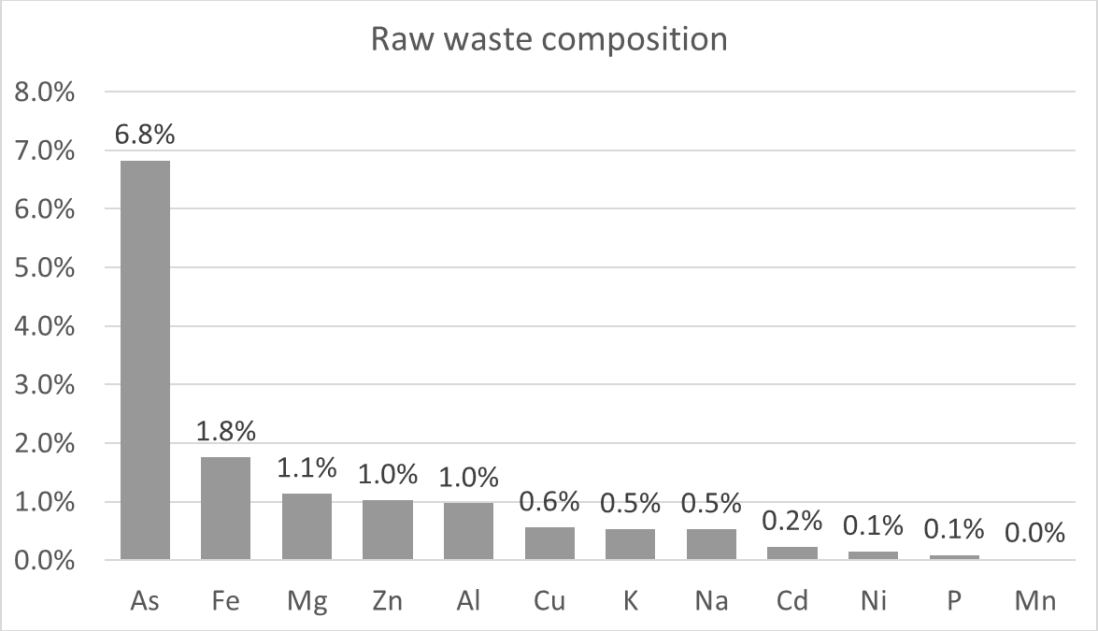


Figure 26. Major elements found in the waste.

The results are close to those reported by Sunyer i Borrell (2013). The main differences are a higher Fe and lower Ni content; the latter being explained by the incorporation of the nickel removal process. The Ca content as measured by this process does not agree with the previous characterization (showing only 6.3% Ca) but only partial digestion was observed, so it seems that gypsum was not fully digested.

The water content of the as-received samples averaged 47% and, after drying at 60ºC, it was reduced to 11%.

6.2 Digestion of the cake

The digestion was not as successful at leaching metals as reported by Sunyer i Borrell (2013) and did not produce the results that had been expected from the preliminary results, which had already shown lower extraction than her study. The recoveries of each major component are shown in Table 11. Whereas Sunyer i Borrel reported 100% As and Fe removal after 5 minutes of leaching with 380 g H_2SO_4/kg cake, only 44% and 49% were achieved in this study after 1 hour with a 600 g H_2SO_4/kg cake ratio.

There are several potential reasons for the results. Not having been able to filter the digestion leachate straightaway, it is possible that initially dissolved metals adsorbed on the solids or precipitated again. Furthermore, the preliminary digestions had been performed with more dilute sulfuric acid, and the difference with them could be explained

because a higher sulfate concentration results in lower gypsum solubility (Azimi et al., 2007). When compared to the study by Sunyer i Borrel, she performed her testwork on the original "neutralization cake" with no mixing with "sulfate cake", so that could justify part of the difference. Moreover, in the cake tested in this study there is a higher amount of Fe than she reported in her study, which also helps to explain the higher requirements. When compared to the results of Smetanin et al., (2007), As extraction is also relatively low. However, their waste had almost no Fe (0.2%) compared to this study.

Table 11. Results of the sulfuric acid digestion.

	As	Fe	Cu	Zn	Al
Recovery (%)	44	49	99	42	22
Concentration (g/l)	8.0	2.4	1.5	1.1	0.6

Therefore, the digestion of the cake has been less successful than others reported in the literature for As mobilisation, but different initial compositions (which are significant especially for Fe) as well as the time passed before filtration can probably explain the difference.

Nonetheless, the goal of this step was to produce an effluent relevant to actual metallurgical processes. The solution resulting from the digestion process resembles those that copper smelters need to treat, and it was therefore deemed quite suitable for further testwork. Arsenic concentration is 8 g/l, which is within the typical range of effluents fed to waste water treatment plants as seen in Table 3. The remaining metals are also within the typical ranges, except for Fe which is not reported in the European IPPC Bureau (2014) report.

6.3 Oxidation

Using permanganate led to a very clear end-point for the oxidation of the solution. After addition of permanganate the solution turns dark brown in colour, but the colour goes back to the original green in a matter of seconds, signalling the consumption of the MnO_4^- ions. The process can be seen in Figure 31, and is completed when the colour change after addition of permanganate remains.

The permanganate consumption needed to complete oxidation was found to be 13.5 g $KMnO_4$ per litre of starting solution. That is, 1.2 times the stoichiometric amount that would be required if all As was present as As(III). If only 50% of the As was As(III) (as reported in the study by Sunyer i Borrell (2013)) then more than 2 times the stoichiometric amount was used. There are other ions present (Fe and Cu, for example) that consume oxidant if they are in reduced states, and would help to explain the consumption of oxidant above stoichiometric As requirements.

6.4 Immobilization performance

The first important requirement that any potential process should meet is to successfully remove arsenic from solution or, in the case of vitrification, to prevent its volatilisation. Arsenic removal performance was calculated using the concentrations and volumes ([As], V) in and out of the precipitation processes as in Equation 4. (Fe8As and AHAP precipitates did not have the "wash" term).

$$As\ \%\ removed = 1 - ([As]_{OUT} \cdot V_{OUT} + [As]_{WASH} \cdot V_{WASH}) / [As]_{IN} \cdot V_{IN} \qquad \text{Equation 4}$$

In the case of the vitrification, the initial cake and the final product were 4-acid digested and analysed to determine the difference between the feed and product As content.

The fraction of arsenic that was successfully precipitated for each method, and the amount of arsenic that was not volatilised during vitrification is shown in Figure 27.

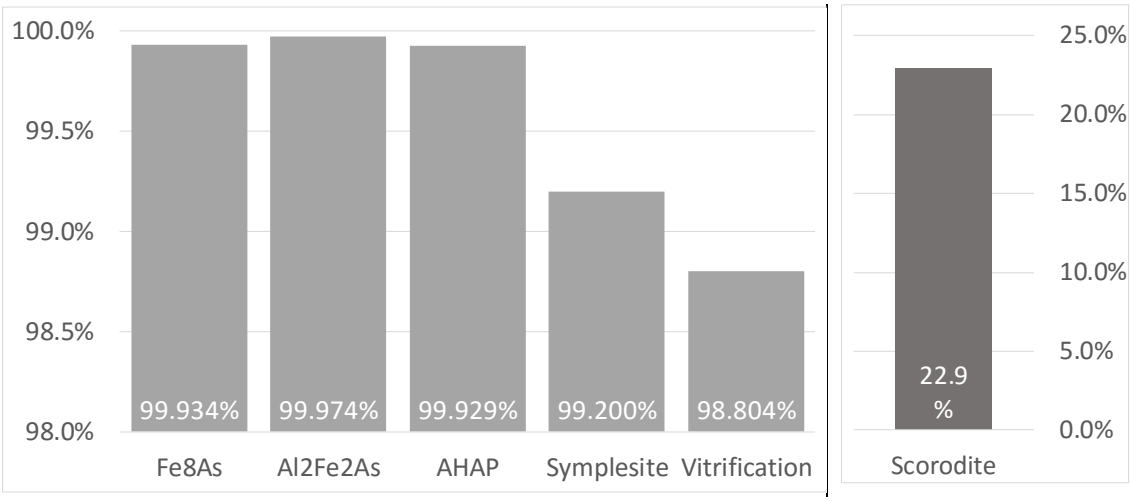


Figure 27. Fraction of arsenic that was removed from solution after precipitations, and that remained in the solid after heating to 1200ºC in the case of vitrification.

The best results were achieved by the Al2Fe2As precipitate, which removed more than 99.97% As. All precipitates synthesised were successful at removing arsenic from solution at quite high levels, except for the gypsum-seeded scorodite.

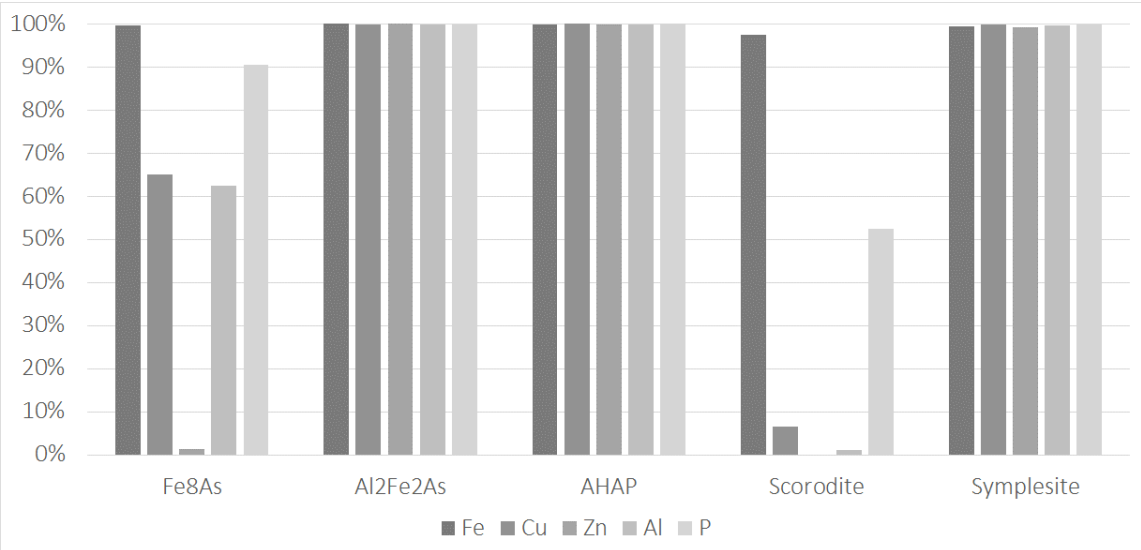


Figure 28. Removal of other elements from solution.

There are some differences regarding the other major components: Fe, Zn and Cu (Figure 28). Symplesite, AHAP and Al2Fe2As have removed almost completely all of those metals, whereas Fe8As and scorodite have more selectively removed As (and Fe), leaving a relatively large fraction of Cu and basically all Zn in solution. This could have potential applications, as the resulting effluent could be a source of Cu and Zn once As has been

removed. In the other cases, Cu and Zn should be first separated if they want to be recovered.

Comments on gypsum-seeded scorodite precipitation

Only 23% of As originally in solution became part of the solid after 5 hours of reaction (Figure 27). The results seem to be explained by the relatively low reaction temperature as it only reached 82ºC during the test, below the minimum reported by Singhania et al. (2005).

Based on the final extraction achieved in this study after 5 hours at 82ºC the trajectory shown on Figure 33 could be assumed and compared to the research that the procedure was based on. The original graph shows the removal efficiency at different temperatures (85 to 100ºC) after seeding with 20 g/l hydrothermal scorodite.

For precipitation at 95ºC, according to Singhania et al. (2005), "*about 80 g/l of gypsum would be required to achieve the same arsenic removal as 20 g/l of hydrothermal scorodite seed*". In this study precipitation with 130 g/l gypsum seed would have been as effective as a hypothetical precipitation taking place at the same temperature using 20 g/l hydrothermal scorodite seed.

The results from the experiment corroborated that scorodite precipitation requires temperatures above 85ºC and not even high seed concentrations can overcome that major factor.

Comments on the vitrification

It was not possible to produce a melt by simple mixing of waste and ground glass. The vitrification process patented by DST claimed that vitrification is possible in the 1100-1200ºC range but this is an anomaly when compared with other examples of vitrification found in the literature, which used higher temperatures for the melting process as exemplified in Table 12.

Table 12. Conditions used for vitrification of waste.

Arsenolite (but claimed to be applicable for arsenical waste in general) is oxidised and transformed to calcium arsenate by addition of manganese oxide and calcium oxide. The resulting mixture is dried and then heated up to 1250ºC in an hour, and stabilised at that temperature for 15 minutes.	(Lalancette et al., 2015)
Lanthanide wastes from 5 to 12 mol% loading. Mixed in a mill for 5 h. Melted in alumina crucible at 1300ºC for 30 min. Quenched by pouring onto a brass mould in air. Heat-treated at 500-800ºC for 3 h to precipitate crystals.	(Kim and Heo, 2015)
Jarosite waste (in a 60:25:39 waste:granite:glass cullet formulation). Melted in alumina crucible at 1400-1450ºC. Quenched in water or poured into steel moulds.	(Pelino, 2000)

Furthermore, it can be seen in typical phase diagrams for glass making compositions that melting in the 1100-1200ºC temperature range is not easily achieved unless there is a high

proportion of flux. That is why sodium carbonate was used as flux in the testwork, as previously mentioned.

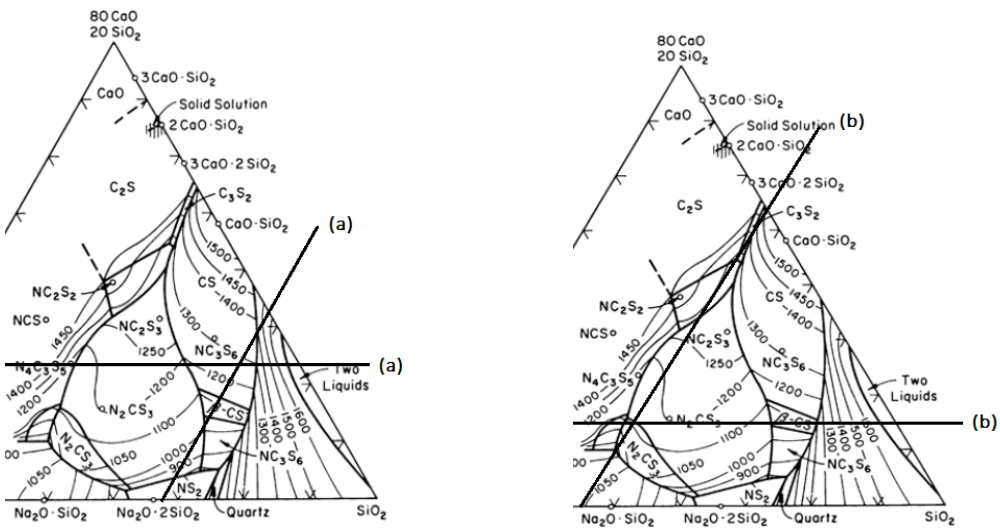
The failure in the first attempt can thus be explained by looking at the phase diagram (a) in Figure 29 and the compositions of Table 13, calculated from the proportions of raw materials and which have been normalised so that those three oxides add to 100%. The Ca content of the cake has been taken into account as part of the CaO content.

The original composition tested would melt at a temperature above 1200ºC if a mixture of the three oxides is assumed. By addition of enough Na_2O, the composition moves into the area shown in (b), ensuring that the melting point is below 1200ºC as proven in the lab when removing the solid residue left by the first experiment. The resulting product was a mixture of glass and the previous crystals and it contains 38% Na_2O, so it was not used for further analysis.

The second attempt tested a different initial composition, (c), which was also correctly predicted to produce a melt, although with lower flux addition. This composition resulted in a product that contains "only" 26.9% Na_2O and which would melt at around 1100ºC.

Table 13. Compositions used for the vitrification testwork.

	%SiO_2	%CaO	%Na_2O	Comment
(a)	67.8	23.5	8.8	First combination. Failed to produce a flowing melt.
(b)	46.9	15.0	38.1	By addition of Na_2CO_3 to the previous crucible which contained solidified material.
(c)	59.5	13.5	26.9	Composition aiming to lower final flux content while preserving melting point below 1200ºC.



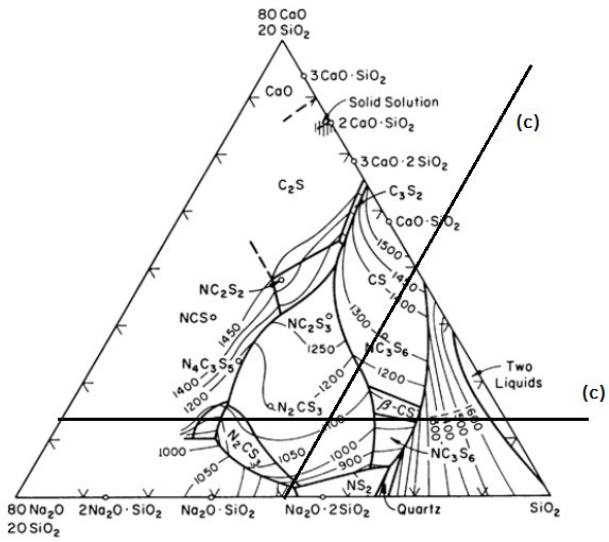


Figure 29. Phase diagrams showing the liquidus temperature for the tested compositions: (a) First attempt, (b) First attempt after adding Na_2CO_3 (c) second attempt.

Analysis of the final successful glass (c) showed it contained 0.575% As. The cake used for the testwork assayed 6.83% As. Taking into account the relative proportions of cake, glass and flux, as well as using results from the thermogravimetric analysis previously performed by the company (the cake loses 25% of its weight upon heating to 1000ºC), it was calculated that 98.8% of As fed to the oven remained as part of the glass and did not volatilise.

This proved the original assumption that no oxidation or further transformation were needed to prevent volatilization. This waste is therefore quite amenable to vitrification without pre-treatment, but higher temperatures are required to avoid flux addition.

Table 14. Arsenic loading expected for no volatilization compared to the actual result.

	Initial mass (g)	Expected final mass (g)	Expected As% if no volatilization	Actual result	Volatilised %
Cake	1.70	1.28	0.582	0.575	1.19
Glass	15.02	15.02			
Na_2CO_3	6.20	3.60 (Na_2O)			
Total	22.92	19.89		19.96	

6.5 Arsenic content

The composition of the precipitates was determined indirectly, by computing the difference between the arsenic mass fed into the process and the arsenic that remained in the filtrate solution and in the wash liquid. The masses were calculated by multiplying the concentrations determined by analysis and the corresponding volumes of the starting solution and the solutions after precipitation. The results are shown in Figure 30.

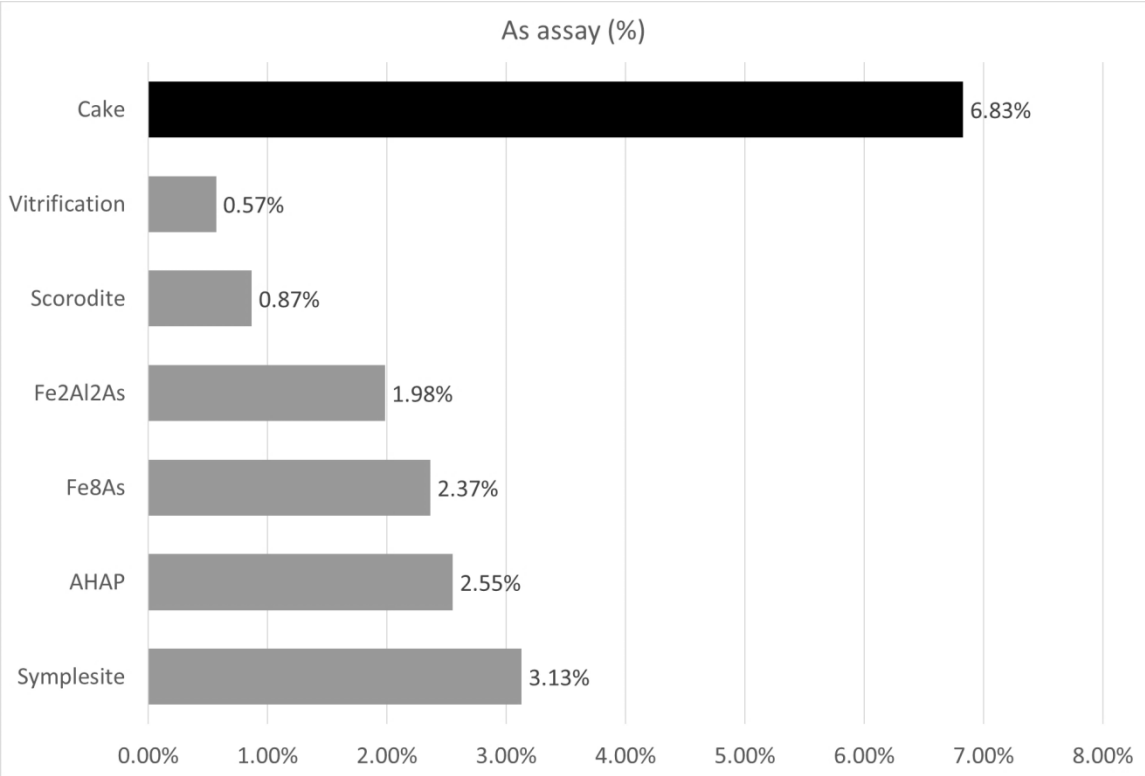


Figure 30. Arsenic content in the solids tested, as well as present in the original waste.

Symplesite has the largest arsenic content, and it could probably be larger if it had been produced at Fe/As ratio closer to the stoichiometric 1.5. The vitrification procedure, on the other hand, needing a large mass of glass and flux for the immobilization, results in a very low arsenic content.

The results highlight the differences between precipitation from laboratory conditions and from actual metallurgical effluents when elements other than arsenic are present, that consume reactants and increase the final solid mass. For example, Ca from milk of lime will precipitate as gypsum, whereas some researchers may use NaOH as base.

This way, whereas researchers may produce ferrihydrite/ferric arsenate solids containing from 26 to 4% As for Fe/As ratios 1 to 16 (Krause and Ettel, 1989) when starting from arsenic acid solutions, acual industrial precipitations starting from "dirty" effluents may lead to precipitates that contain only around 1% As (Aurubis Hamburg smelter, according to European IPPC Bureau (2014)) and the Fe8As precipitated in this study contains "only" 2.4% As.

6.6 Leaching behaviour

Leaching behaviour will be discussed in two ways: (1) based on the mg As/kg released for each method, and comparing it with the legal requirement of hazardous landfills (25 mg/kg release) and (2) by the fraction of arsenic released, as each solid has different arsenic content and similar leachate concentrations could hide a much higher relative release.

Figure 34 and Figure 35 show the results from each perspective. The first observation is that the original cake waste is indeed very hazardous, potentially releasing above 10% of its As content in the first 24 hours after equilibration at pH 8.2. It has much better performance at its natural pH (around 12), but As release is still not low enough for landfill acceptance even at that high pH value, which cannot be expected from typical landfill leachates anyway.

This corroborates how a simple, single-condition test would be partially masking the extremely hazardous nature of the waste, and makes it clear that it is necessary to test the leaching behaviour following tests in the style of the European standard EN 14429, that asks for assessing release on the full pH range.

The results show that all methods released less arsenic than the original waste when pH was below 9, which is the maximum value that can be expected in landfills. There are, however, huge differences in performance between the different methods and all methods but two failed to render the waste acceptable at landfills according to European requirements.

Vitrification showed quite poor results, most likely for the reasons explained before (high flux content), even though it did result in less leaching at near-neutral pH than the original waste. Its arsenic release is high both in mg/kg and %As terms, even though it is clearly larger in relative terms as it has the lowest arsenic content of the methods tested. The conclusion is clear: for waste vitrification higher temperatures should be used and flux avoided.

The results of the simple ferrihydrite/ferric arsenate precipitation, Fe8As, were surprisingly bad. Even after considering that the pH conditions that were tested (pH 3.2 and 8.4) are not the most favourable, arsenic was released in a much larger fraction than was expected given the literature review. In fact, the concentration in solution was similar to that expected for an Fe/As ratio of 1 as shown in Figure 36. First of all, the procedure should be repeated with a precipitate washing step, as it may be that pore water remaining after filtering distorted the results too much. If the repetition still showed poor results, it could be attributed to the fact that a “dirty” effluent was used, and that arsenic, besides ferric arsenate/ferrihydrite, precipitated into other compounds which show lower solubility, such as calcium or copper arsenate.

In the same way, arsenate hydroxyapatite resulted in large As release and even the best results obtained at its natural pH (8.1) were not suitable for disposal. The poor AHAP leaching behaviour observed in this study may corroborate that Fe hinders the stability of the product, as claimed by Shan (2008). Therefore, it may still be applicable to the original non-Fe effluents, but it has failed to produce a safe solid from the starting Fe-containing solution.

Gypsum-seeded scorodite precipitation (at 82ºC) presented mixed results. Even though there is too-high release at the pH values reached during the bottle tests, they were in fact quite extreme and not within the landfill range. Arsenic release was not among the highest and, according to the literature, it should be lower for the more landfill-relevant pH values in-between (Figure 36). More leaching tests would have been performed for this 82ºC scorodite had it not been for the markedly poor removal, which actually rendered the

process useless for the purpose of arsenic immobilization, in these specific conditions tested.

Two precipitation methods were undoubtedly successful: symplesite (starting from a ratio of Fe(II)/As = 4) and the two-step Al/Fe precipitation (Al2Fe2As). The solids from both methods would meet the legal requirements for hazardous landfills, as they leach less than 25 mg/kg of arsenic when the test is performed at their natural pH (6.5 for symplesite and 7.8 for the two-step precipitation).

Moreover, the fraction of arsenic released by these methods in the near-neutral pH range was also the lowest of all tested, below 0.1%. Symplesite, in fact, had the highest As content of the methods tested, only a bit less than half of the original waste (3.13% instead of 7%), but the fraction of arsenic it released for the pH relevant for disposal is 365 times smaller than the waste. The Al2Fe2As precipitate also has a relatively high As content (almost 2%, or 3.4 times less than the cake) and it released 290 times less As in that range.

The results for these two precipitates are as expected from the literature, and it can be extrapolated that their behaviour under more acidic conditions would be even less arsenic release.

Comments on analytical uncertainty

The standard deviation of arsenic after analysis of the blank leaching tests in triplicate was 0.24 mg/l, which is certainly much larger than the achievable theoretical detection limit of ICP-OES instruments (50 µg/l). The reasons probably include (1) some cross-contamination from the cleaning utensils and not complete washing of filters, beakers, etc. (2) the reagents that were used were only “reagent grade” and, for example, the lime used for precipitations contains <0.0003% As which adds a certain noise to the measurements.

The uncertainty, nevertheless, was clearly low enough to be able to decide whether a leachate is above or below the EU legal threshold of 2.5 mg/l for acceptance at hazardous landfills (Table 4). The results also showed good repeatability, as shown by the second batch of leaching tests on symplesite and Al2Fe2As that showed consistent results.

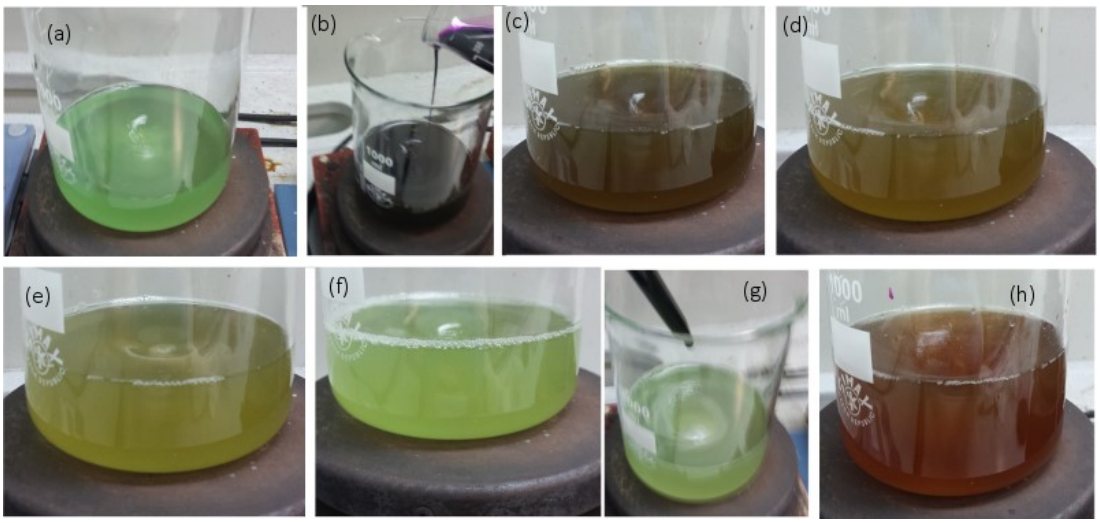


Figure 31. Oxidation process: (a) non-oxidised solution, (b) permanganate addition, from (c) to (f) the dark colour or permanganate fades away as it gets consumed, (g) new addition of permanganate leads to permanent colour indicating oxidation is complete (h).

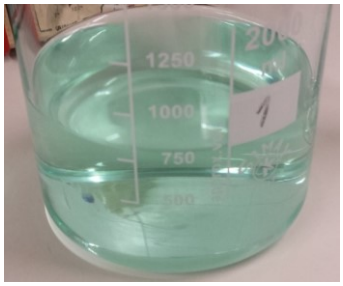


Figure 32. The filtrate from scorodite precipitation still contains dissolved metals, as it is evident from its colour.

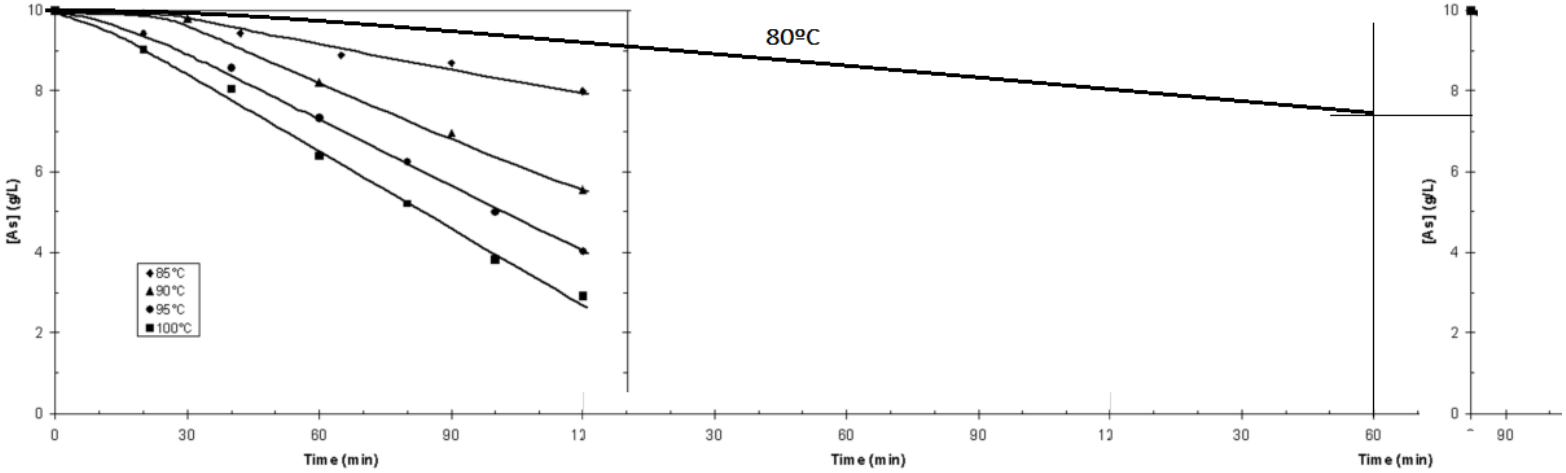


Figure 33. Graph showing As remaining in solution as a function of time for 85, 90, 95 and 100ºC (Singhania et al., 2005), together with the superimposed assumed trajectory of the 5-hour 82ºC test.

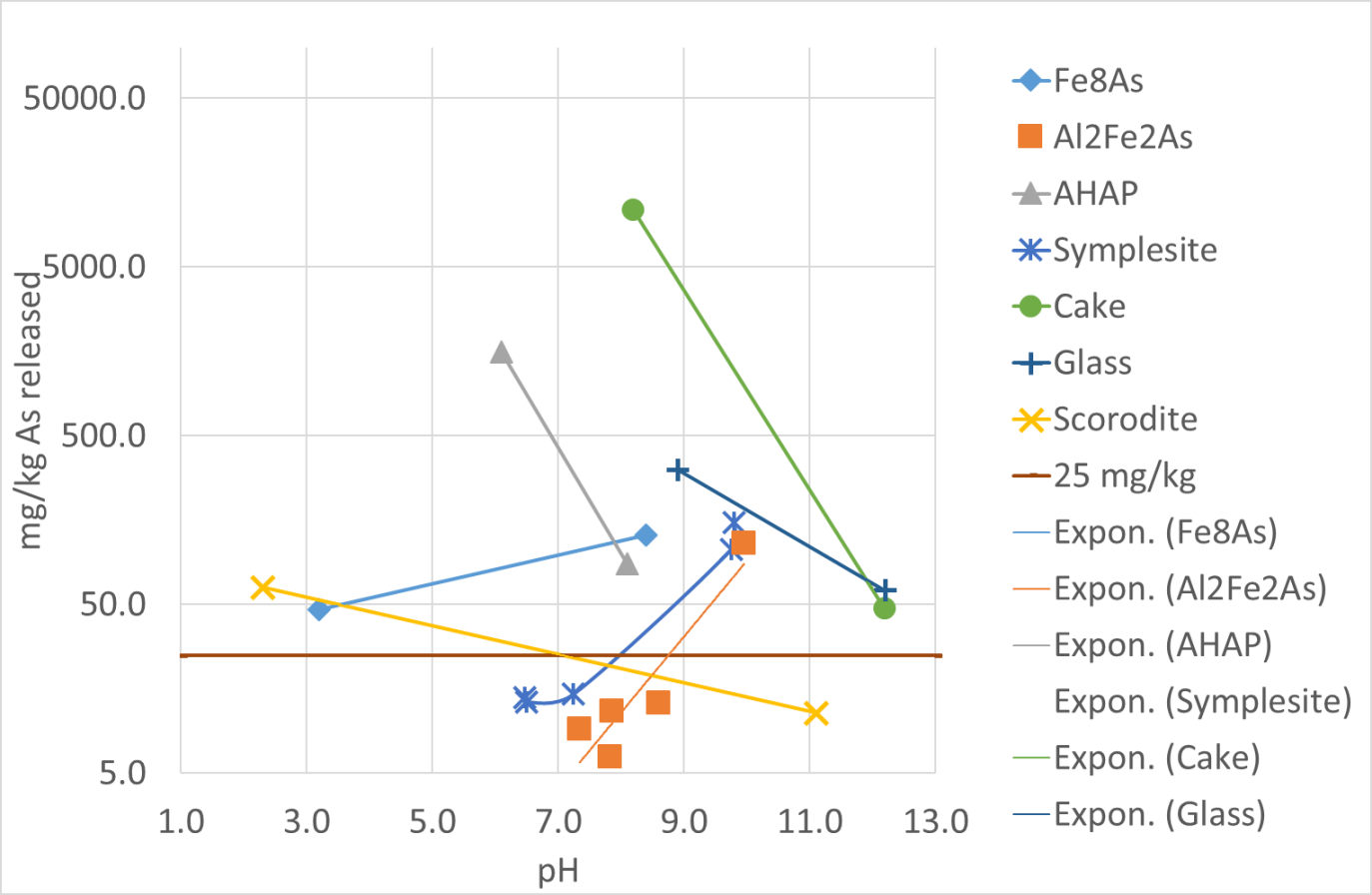


Figure 34. Arsenic released calculated as mg/kg of dry sample mass. The line at 25 mg/kg shows the maximum limit for acceptance at hazardous landfills. <u>The lines do not actually show the behaviour in-between the values, they only join each precipitate's values together for easier reading.</u>

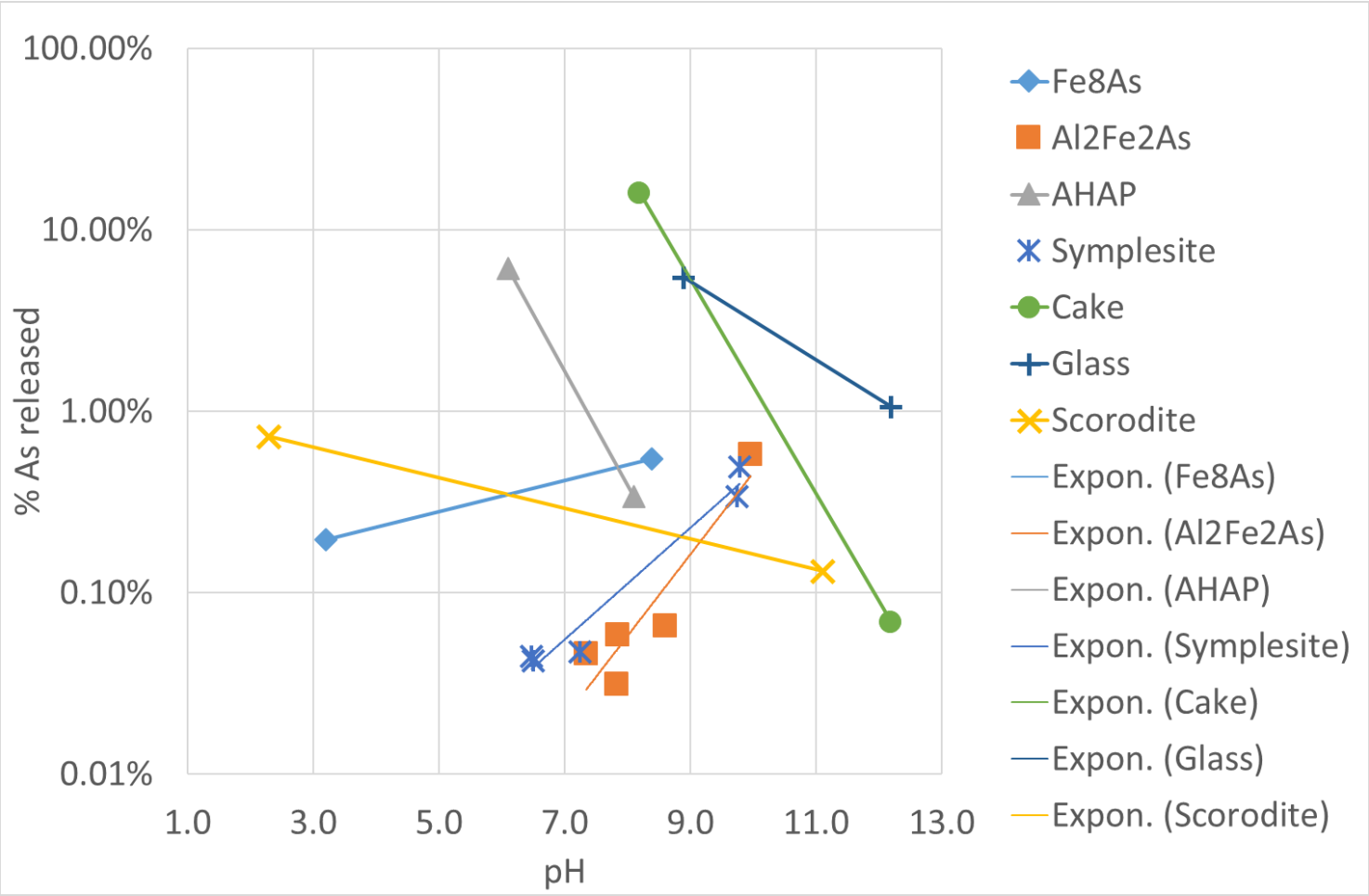


Figure 35. Arsenic fraction released by each method at the tested pH values. The lines do not actually show the behaviour in-between the values, they only join each precipitate's values together for easier reading.

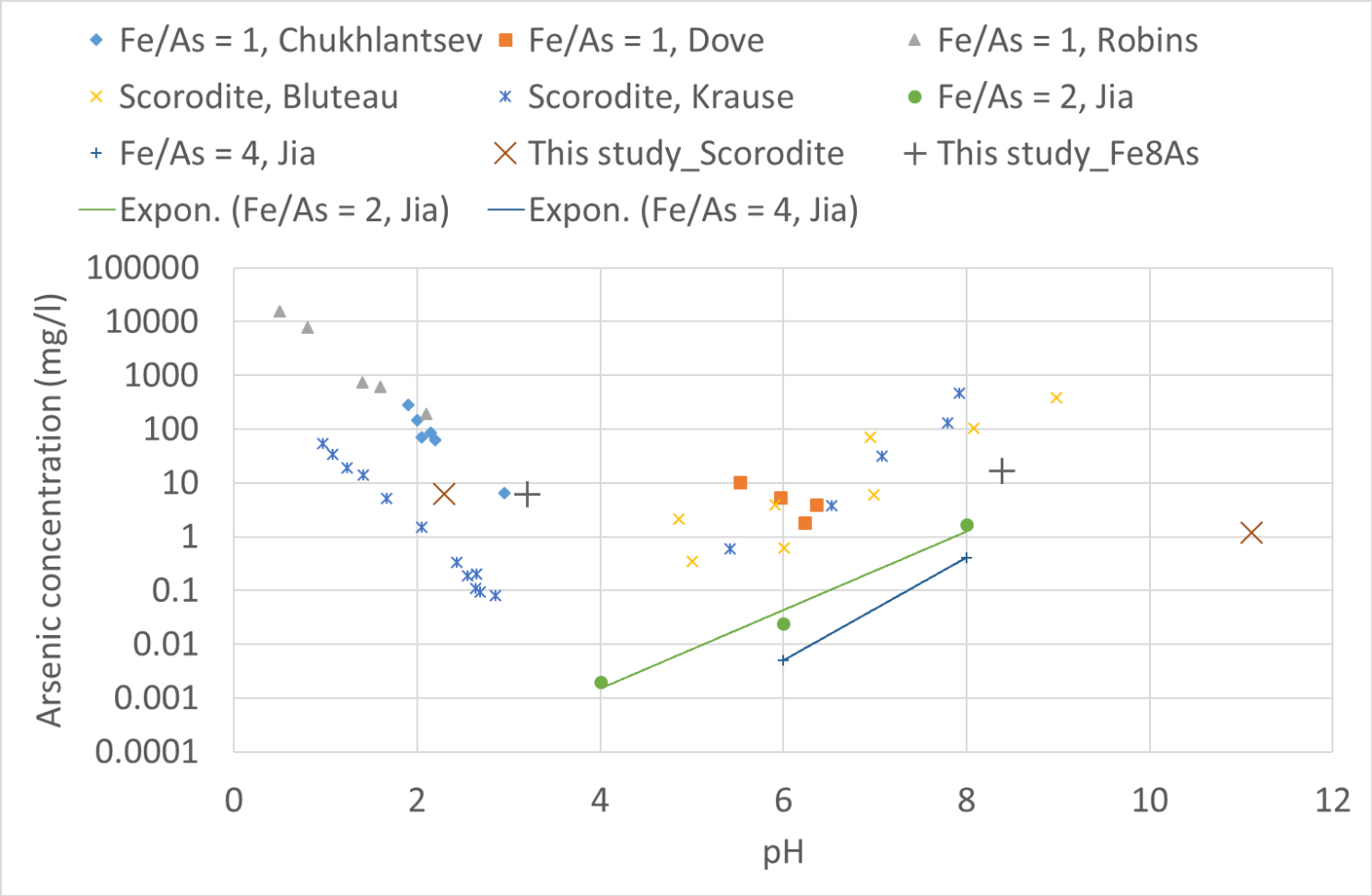


Figure 36. Scorodite and ferrihydrite (mostly of Fe/As = 1) solubility values. The larger cross and plus sign are the concentration in solution found in this study (note scorodite is gypsum-seeded and that different L/S ratios were used).

6.7 Potential process for As removal

Based on the results from the leaching tests, either symplesite or two-step Al/Fe precipitation should be further studied. They are both precipitation methods that would require similar capital investments in the form of tanks, pumping and other auxiliary equipment. It should also be possible to retrofit an existing precipitation process to produce these new precipitates.

As an indication of the CAPEX for a new facility, Aurubis Pirdop's treatment plant costed 10 million € and consists in a three-stage precipitation process: gypsum, metal hydroxides and arsenic precipitation by lime neutralization with addition of coagulants/flocculants (European IPPC Bureau, 2014).

A preliminary estimation of operational expenditure could be made based on this work's bench-scale consumptions of oxidant, reactants and lime for neutralization, which are summarised in Table 15. The flow rate used for calculations is assumed at 100 000 m^3/year, thought reasonable according to examples provided in the BREF report (European IPPC Bureau, 2014). The reagent consumptions have been recalculated based on commonly used iron and aluminium salts: iron(II) sulfate heptahydrate, iron(III) chloride hexahydrate and aluminium(III) sulfate heptahydrate.

Table 15. Reagent requirements from the lab experiments. Yearly consumption assuming an effluent with 8 g/l as in the testwork, and flowrate 100 000 m^3/year.

Consumption	Symplesite		Two-step Al-Fe	
	g/l	tons/yr	g/l	tons/yr
$KMnO_4$	13.5	1350	13.5	1350
Fe(II) sulfate heptahydrt.	120	12000	-	-
Fe(III) chloride hexahydrt.	-	-	46.5	4650
Al(III) sulfate heptahydrt.	-	-	34	3400
Lime	82	8200	98	9800
Solids produced, with 50% water		51000		81000

The unit prices in Table 16 have been computed from prices found on the sources cited as notes, which have been updated to 2016 prices by application of the "Producer prices, industrial chemicals" index from several years ("Economic Indicators," 2016), and subsequently converted to euros at current exchange rates.

Therefore, the symplesite process would be the cheapest of the two alternatives at 2.8 million € per year of reagent costs. Assuming reagent costs amount to 80% of the total operating costs (as for scorodite according to Filippou and Demopoulos, (1997)), the total should be close to 3.5 million €/yr.

For solids containing 3.13% As and 50%, there would be a 51 000 t/year product. The costs of the process would thus amount to around 67 €/ton (lower than cement solidification or vitrification). It would, however, more than double the amount of waste produced, as the current process produces a 7% As solid. It should be possible to optimise the reagent consumption for the symplesite process, as the stoichiometric ratio is lower than the Fe/As = 4 that was used.

Table 16. Calculated operational costs per year.

Yearly costs	Unit cost assumed (€/ton)	Symplesite (million €)	Two-step Al-Fe (million €)
$KMnO_4$ [1]	590	0.8	0.8
Fe(II) sulfate heptahydrt.[2]	165	2.0	-
Fe(III) chloride hexahydrt.[3]	330	-	1.5
Al(III) sulfate [4]	348	-	1.3
Lime[5]	52	0.4	0.5
Total reagents cost		2.8	3.7
Total OPEX (80% reagents)		3.5	4.6

One advantage of the two-step process that could justify its selection would be the higher As removal efficiency and the fact that no oxidation prevention measures need to be taken. However, higher removal efficiency for symplesite may be achieved by optimization of the process as well.

The current treatment costs are not known, so the values reported for Aurubis Pirdop in the European IPPC Bureau, (2014) will be considered, after adjusting for a production similar to that from the example above (Aurubis processes 2090 t As/yr but the example above only treats 800 t/yr, so all amounts have been reduced accordingly in Table 17). The unit price for 70% hydrogen peroxide is mentioned in the same BREF report to be 600 €/ton. Note that iron chloride is used in Aurubis as flocculant for several steps. Had it been used for arsenic precipitation, the Fe/As ratio is only 2.3, far from Fe/As > 4 for safe ferrihydrite/arsenate precipitation.

Table 17. Consumptions and cost estimates for Aurubis, after adjustment for the same amount of As.

	H_2O_2	$FeCl_3$	Lime	Total OPEX (assuming reagents 80%)
tons/year	1600	6720	16145	
million €/year	1.0	2.2	0.8	5.0

The operating costs of the symplesite process without optimization would thus not be far away from those of current practices, especially taking into account that it has also successfully removed most of the other elements in solution and could be used as a metal removal step. Capital costs are not expected to be different from other treatment options, and although oxidation of the Fe(II) source should be prevented, it does not seem far-fetched to imagine that retrofitting the existing precipitation process is possible.

[1] 2011 world market price from http://nwtaac.org/the-truth-about-chinas-dumping-practices/
[2] 2005 price from http://www.icis.com/resources/news/2005/12/02/517817/chemical-profile-ferrous-sulfate/
[3] 2005 price from http://www.icis.com/resources/news/2005/12/02/516155/chemical-profile-ferric-chloride/
[4] 2004 price from www.icis.com/resources/news/2004/12/03/633745/aluminum-sulfate-prices-rise-with-demand-and-costs/
[5] 2000 price from icis.com/resources/news/2001/09/24/149931/us-lime-market-faces-upward-pricing-pressure/

7 Conclusions

7.1 Research summary

The literature review led to the identification of a great number of proposed As immobilization methods. Many of them have only be tested at the bench scale starting from synthetic solutions. Only a few are applied industrially, especially calcium arsenate (in European smelters) and low temperature precipitation with iron. More recently, scorodite processes and vitrification have been introduced. Other methods such as cementitious solidification are widely applied for hazardous elements immobilization in different types of waste.

The testwork consisted in trying to immobilise an actual hazardous metallurgical waste applying promising methods selected from the literature review. Solids stabilisation by vitrification was tested on the original waste, but was not successful for the specific conditions used.

The waste was digested to produce an effluent equivalent to those found in copper smelters. On that solution, more relevant to industry than artificially prepared ones, alternative precipitation methods were tested. Two methods were found to be the most promising for the effluent: symplesite precipitation and a two-step Fe and Al precipitation.

Both removed more than 99% As, but the two-step process was closer to achieving a fully safe effluent, whereas the symplesite precipitation, at only 99.2% removal would still leave too much As in solution for discharge. In terms of leaching behaviour, within the pH range that can be expected for landfill leachates during 24-hour bottle tests, arsenic leaching was reduced more than 290 times for the two-step solids and 350 times for symplesite when compared to the original waste.

These two options result in solids that could be placed in hazardous landfills according to EU legislation, and they have the potential to successfully replace the existing process. A preliminary cost estimation shows that symplesite would meet the goal of being a good replacement of existing precipitation processes, by maintaining or even decreasing operational costs while producing a safer solid able to be disposed in landfills.

At the conditions tested, not even the 2 best options have passed the limits to be placed in non-hazardous landfills, but there is likely room for improvement and optimization of those processes and further modifications could result in lower leaching.

7.2 Suggestions for further research

7.2.1 Long-term dynamic leaching tests

The literature review has stressed the need to determine the leaching behaviour of the alternative immobilization options under conditions representative of landfills. Tests such as the long-term EN 14405 percolation test should be performed, and ideally using leachate taken from landfills. Ageing tests could be performed to asses long-term leaching as well.

The behaviour on the full pH range should be characterised with an EN-14429 type of test.

7.2.2 Pilot and industrial scale operation

Only very simple batch tests have been performed that, although promising, still need further corroboration. Continuous testing at, ideally, pilot-plant scale should be performed to validate the bench-scale results.

7.2.3 Improved or alternative processes

Some of the discarded precipitation approaches could potentially have good results for this effluent, so they could be tested as well if their more complex synthesis methods were not a problem.

The vitrification testwork could be improved. Firstly, melting should be tested without flux at higher temperatures in another furnace. Secondly, the lowest Na_2O proportion for melting below 1200ºC should be determined, and leaching behaviour tested for that composition.

Testing scorodite precipitation at higher temperature, followed by leaching tests in the 7 to 9 pH range should be undertaken. Two-step processes could be tested with symplesite as well, as well as optimising the Fe(II) consumption.

The possibility to combine several methods could also be considered. As mentioned, there is an agreement between EcoMetales and Dundee Sustainable Technologies to complement scorodite precipitation with vitrification so it may well be that the best approach is to produce first a safer precipitate and then vitrify it. This would of course increase the costs considerably.

7.2.4 Processing characteristics

Properties such as filtering should be tested and their associated costs considered. It was clear during the testwork that there was a qualitative difference in the ease with which the different solids filtered. For example, AHAP filtered much faster than Fe8As. If all other conditions are the same, this is an important parameter as simpler and faster dewatering will lower processing costs.

7.2.5 Life-cycle analysis

When looking for sustainable processes, it is important to take into account all the effects produced by it, including those related to inputs and outputs that could be missed in a simple analysis. A life cycle analysis (LCA) should be performed to compare if the different reactants and the energy required can be really provided sustainably to the location of the treatment plant.

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Annex 1. Some literature values of solubilities and arsenic release

	Solubility product	Arsenic release at pH:						Comments		
	-log Ksp	(mg/l)							As %	Source
pH		5	6	7	8	9	>12			
Coprecipitation Fe/As = 4		0.09	0.1	0.2	0.7	1.2				Jia
Two-step Fe2As1Al2		0.03	0.06	0.06	0.2	0.2				Jia
High-T scorodite	24.17 to 25.87	0.3		5.9	463				32.5	Krause
Low-T seeded scorodite										
By simultaneous oxidation				3.14		352				Fujita
Bioscorodite										
Scorodite-Mansfieldite, 4% Al					8.4			After 40 days		Berre
Iron arsenate, 84% Al substitution	2.74			40						
Arsenate hydroxyapatite (high As)				0.52						Zhang
AHAP (P/As = 5)									7.1	
AHAP (low As)			2.8				0.02			Shan
As-Schwertmannite	13.5	0.82						at pH 4	6.0	Raghav
Symplesite	33.25	0.023			0.07	7			25.4	Johnston, Raghav
Yukonite		5.3		3.1	7.5			After 132 days, oxic conditions	24.4	Bohan
Beudantite	10.53	0.02							10.5	
Natroalunite 8.5% AsO4			0.37		0.01				4.6	
Natroalunite 19.5% AsO4			7.8						10.5	
Tooleite			>20		>30		>20		25.0	Raghav, Opio
Cement solidification							<8		-	Leist, Vandecasteele
Vitrification										

Annex 2. Analysis results

Volumes of the lixiviant additions for the leaching tests can be found in the next annex.									
		nm =	214	396	194				214
	V(ml)		Zn (mg/l)	Al	As	Cu	Fe	Mn	P
Fe8As in	50		1146.72	569.57	8067.97	1470.18	2306.10	34.60	132.13
Al2Fe2As wash	575	B1	0.03	2.37	0.26	0.02	0.00	3.25	0.02
Scorodite wash	928	B2	142.04	32.79	408.47	72.57	9.89	211.43	4.33
Al2Fe2As out	621	A3	0.02	1.05	0.31	0.11	0.00	5.16	0.04
AHAP in	200	A4	998.25	509.11	7296.47	1223.83	2423.77	35.97	141.18
Blank (pH 8.2)	150	L18	0.15	0.02	2.11	0.07	0.23	0.00	0.00
Scorodite in	500	A6	1013.00	524.74	7426.45	1259.90	2456.65	36.87	145.53
Scorodite out	835	A7	794.58	274.02	2972.77	624.92	83.56	1076.36	36.72
Symplesite in	200	A8	1027.37	530.56	7461.47	1265.82	2453.76	36.93	145.85
Symplesite out	687	A9	1.21	0.30	8.14	0.28	25.55	37.80	0.08
Blank Storage	300	A12	0.03	0.00	1.51	0.01	0.05	0.01	0.01
Fe8As out	182	A1	310.97	58.92	1.46	141.06	40.58	428.39	3.47
Al2Fe2As in	200	A2	957.98	428.47	6576.34	1011.00	2142.18	28.93	118.27
Symplesite wash	832	B3	1.13	0.27	7.62	0.44	16.07	23.33	0.01
Fe8As (8.4)		L1	2.30	0.55	16.97	0.99	3.07	0.64	0.18
Fe8As (3.2)		L2	189.33	64.14	6.07	120.93	271.92	236.72	4.17
Al2Fe2As (10)		L3	0.04	5.63	11.68	0.03	0.04	0.07	0.03
Al2Fe2As (7.8)		L4	0.00	0.01	0.44	0.00	0.00	0.05	0.02
Al2Fe2As (7.9)		L5	0.03	0.13	1.35	0.00	0.01	2.84	0.00
AHAP (6.1)		L6	0.00	0.03	152.01	0.00	0.01	0.16	6.99
AHAP (8.1)		L7	0.00	0.00	8.72	0.00	0.01	0.00	0.41
Scorodite (11.1)		L8	0.00	0.03	1.20	0.02	0.01	0.00	0.09
Scorodite (2.3)		L9	0.08	0.05	6.30	0.03	0.00	0.01	0.20
Simple (9.75)		L10	0.00	0.25	8.50	0.01	0.02	0.01	0.06
Simple (9.8)		L11	0.58	0.42	18.85	0.18	0.55	0.11	0.09

Simple (6.5)		L12	0.03	0.02	1.31	0.01	0.02	0.10	0.00
Vitrified (8.9)		L13	0.31	0.66	28.67	0.13	0.39	0.12	0.05
Vitrified (12.2)		L14	0.43	2.47	6.06	0.21	0.64	0.12	0.01
Cake (8.2)		L15	0.06	0.33	1109.22	0.05	2.98	0.10	0.12
Cake (12.2)		L16	0.39	0.18	5.24	0.03	0.02	0.00	0.00
Blank (4.2)		L17	0.03	0.02	0.83	0.01	0.03	0.01	0.00
AHAP out	648	A5	0.09	0.16	1.59	0.02	0.45	0.07	0.04
Blank		L18A	0.00	0.02	0.13	0.00	0.00	0.00	0.00
Blank		L18B	0.00	4.46	0.70	0.16	3.13	0.17	0.00
Blank		L18C	0.00	0.00	0.27	0.00	0.00	0.00	0.00
Al2Fe2As (7.8)		L4	0.05	0.70	0.81	0.00	0.60	4.14	0.00
Al2Fe2As (7.9)		L5	0.01	0.33	0.99	0.00	0.00	5.80	0.00
Simple (6.49)		L20	1.70	0.21	1.38	0.00	0.03	80.47	0.09
Al2Fe2As (7.34)		L22	0.16	0.17	0.92	0.00	0.03	23.80	0.00
Symplesite (9.75)		L10	0.01	0.95	12.93	0.00	0.00	0.03	0.00
Symplesite (9.8)		L11	0.03	0.70	15.25	0.02	0.36	0.28	0.12
Al2Fe2As (8.6)		L21	0.00	0.59	1.32	0.00	0.02	1.97	0.04
Symplesite (7.24)		L19	0.21	0.12	1.43	0.00	0.04	18.72	0.00
Fe8As final		A14	487.85	1.99	0.52	174.40	23.09	628.54	3.48
Cake (12.2)		L16a	1.37	0.39	4.20	0.32	0.36	1.08	0.00
Cake (12.2)		L16b	0.35	0.17	4.33	0.04	0.01	0.03	0.00
Cake (8.2)		L15	0.08	0.15	1022.15	0.06	3.03	0.10	0.12
Vitrified digestion (ppm)	-	D1	810.46	8250.19	5746.97	399.02	3504.25	35.37	123.33
Cake digestion (ppm)	-	D2	10239.20	9702.37	68293.30	5580.56	17580.90	238.77	882.94

Annex 3. Leaching behaviour test conditions

The acid used was HNO_3 and the base NaOH, of different concentrations according to the needs.							
		Wet solids (g)	Moisture (g)	Lixiviant addition (ml)	mol H+	mol OH-	Final pH
L1	Fe8As	5.73	1.23	43.8	0.00000	0.00750	8.39
L2	Fe8As	5.73	1.23	43.8	0.00000	0.00000	3.20
L3	Al2Fe2As	27.22	12.22	137.8	0.00700	0.01250	9.96
L4	Al2Fe2As	27.22	12.22	137.8	0.00000	0.00000	7.83
L5	Al2Fe2As	27.22	12.22	137.8	0.00000	0.00000	7.85
L6	AHAP	17.76	2.76	147.2	0.03850	0.00000	6.10
L7	AHAP	17.76	2.76	147.2	0.00000	0.00000	8.10
L8	Scoro	17.76	2.76	147.2	0.02600	0.01800	11.11
L9	Scoro	17.76	2.76	147.2	0.00000	0.00000	2.30
L10	Sympl.	10.69	0.69	99.3	0.01150	0.01250	9.75
L11	Sympl.	10.69	0.69	99.3	0.01200	0.01250	9.79
L12	Sympl.	10.69	0.69	99.3	0.00000	0.00000	6.50
L13	Vitrif	6.50	0.00	65.0	0.03400	0.00150	8.93
L14	Vitrif	6.50	0.00	65.0	0.00000	0.00000	12.20
L15	Cake	16.85	1.66	150.2	0.07650	0.00000	8.17
L16	Cake	16.85	1.66	150.2	0.00000	0.00000	12.20
L17	Blank	0.00	0.00	150.0	0.00000	0.00000	4.22
L18	Blank	0.00	0.00	150.0	0.00000	0.00000	8.20
L19	Sympl.	6.4	0.38	61.0	0.00000	0.00020	7.24
L20	Sympl.	6.4	0.38	60.0	0.00006	0.00009	6.47
L21	Al2Fe2As	12.7	5.73	64.0	0.00000	0.00113	8.58
L22	Al2Fe2As	12.7	5.73	64.00	0.00210	0.00000	7.34