

Potential Uses of Copper Wastes in the Building Sector: Inertization and Added Value Solutions [†]

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Abstract: Mining activity is the second biggest producer of waste in the European Union (EU), so to develop processes that allow the reuse of waste and the consequent creation of markets for these secondary raw materials are relevant for a desirable transition to a circular economy. Copper waste such as cakes, tailings, pyrite roasting residues, or slags present very different physical characteristics and hazards. There are two important aspects to consider for the residue of hazardous determination and its reuse: the particle size and the leaching behavior. Also, the reactive or non-reactive property of the waste depends on their origin, which is important for new applications. Based on these parameters (and other specifics for each application), the intention of this paper is to review and study the different applications of copper residues, aiming for new possibilities of cement-based construction materials with added value that allow to economically justify the use of cement.

Keywords: arsenic; copper wastes; cement; mortar; concrete



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1. Introduction

In 2018, mining produced 635.5 Mt of waste, which represents 24% of all waste produced in the European Union (EU). Only the construction sector presents a higher value, 37% [1]. On the other hand, copper mining estimates that 1 ton of copper metal production generates about 130 tons of mining and metallurgical waste (tailings and slags) [2].

Despite the fact that Directive 2006/21/EC [3] has served to add pressure to this sector, there is still room for improvement in the regulatory aspect of construction materials in mining operations since currently all this waste is treated and deposited in the mining area [4] with subsequent integration in the environmental restoration plan. On the other side, an increase in the use of mining waste in the construction sector may contribute positively to the decrease in the consumption of raw materials by this sector.

These practices have already been carried out in very different ways. The use of copper tailings as a filler for the mining chambers, known as cemented paste backfill, is the most common one [5]. This technology contemplates the filling of mining chambers with a paste composed of copper tailings together with a hydraulic binder in low proportions to provide some additional structural integrity. On the contrary, the use of the copper tailings as a filling aggregate (for the construction sector) is not frequently considered due to the need to stabilize the waste to reduce its danger [6]. Therefore, investigations to apply in mortars [7–9], concretes [10–13], and ceramic products [4,14,15] have been more frequent. Another option is the inclusion in geopolymer mixtures [16–18], which are materials bound

with a material rich in aluminum oxides and silicates capable of developing resistance when activated with an alkaline solution. These can be metakaolin, fly ash, or slag [19]. This option has been extensively studied since it is shown as a potential alternative to ordinary Portland cement [20]. In addition, there is the possibility of partially or totally substituting cement and/or aggregates by other types of waste or different natural materials to obtain a product called composite [21,22] that, despite not meeting the standards required by European legislation relating to construction materials, it has a good physical, chemical, and mechanical behavior.

All these applications have a double purpose. On one hand, they intend to inert or stabilize the pollutants present in the waste, and on the other hand, to develop a new construction material.

The fixation of copper residues has already been studied and has been applied for years on an industrial scale. The main objective is to reduce the danger of waste and increase its chemical stability. In general, precipitation processes with additions of lime, iron, or sulphides are used [23] when the streams present pollutants in solution. In case of solid waste, cement can be used as a form of encapsulation proven as effective, but presents a high cost and high carbon footprint (derived from cement production) [24].

The use of copper waste as construction material has two great advantages that will drive the growth of this practice in the coming years: it reduces the consumption of primary raw materials for construction material manufacturing and allows the valorization of the copper waste as a secondary raw material in construction applications. On the contrary, there is a great disadvantage: the extensive European regulations on construction materials limiting the use of this kind of waste in order to maintain high quality standards; not because of its origin but partly because of its composition and mainly because of its properties.

This paper aims to review the requirements of different construction materials according to the regulations, without going into depth in the different applications of each material in particular, with the aim of determining the essential requirements, the greatest barriers and solutions, addressing the potential evolution of each material.

2. General Characteristics of Copper Waste

In general, copper mining waste is divided into several large groups (Figure 1): inert waste from exploitation, tailings [25], and pyrometallurgy products [26]. Inert waste already has an internal reuse route and they are currently used for the construction of roads and dams or as filling aggregates.

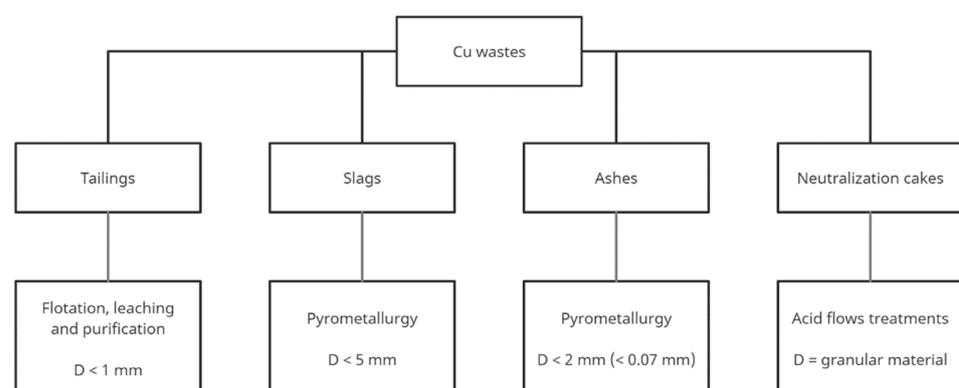


Figure 1. General classification of copper mining waste.

Tailing is the waste generated in the concentration of copper, either through flotation or leaching and purification processes. In the case of flotation residues, these have high amounts of silicon and iron and less, yet more variable amounts of aluminum, calcium, zinc, lead, copper, magnesium, potassium, and contaminants such as arsenic or bismuth [27–30]. The particle size depends on many factors and is a characteristic studied to optimize both

flotation and leaching, but for the purposes of construction materials it can be accepted as less than 1 mm [11].

The copper concentrated by flotation is usually treated by pyrometallurgy generating three types of waste: cakes, slag, and dust. Slag is the main waste from smelters and its composition depends on the origin and composition of the mixture of concentrates used to feed the furnace, as well as the reagents and fluxes used in the process. In general, they are made up of iron silicate with lower amounts of aluminum, calcium, magnesium, potassium, etc. [31–37]. Its particle size is less than 5 mm [27,38]. Although the dust is recovered in much smaller amounts compared to the previous residues, they are of great importance. On the one hand, many of the toxic elements are recovered in the dust collected from the furnace gas stream because they volatilize during the melting process. On the other hand, its size is very small (microns), which makes it a health and environmental risk. Dusts are mainly composed of oxides and sulfides of lead, zinc, iron, tin, copper, and arsenic [39]. It is common for the furnace gas stream to be washed with water, allowing the generation of sulfuric acid and recovering of some of the recoverable metals [26,39–42]. In such a case, an acid stream with valuable metals and also with dangerous compounds (As) are set with lime, carbonates, sulfides, iron, or cement as already explained.

Furthermore, in Spain, a concentration system by roasting pyrites was common in the 19th century. These residues are currently being investigated for exploitation assessment. They have very diverse compositions based on silicon, iron, copper, sulfides, and lead, but with high amounts of arsenic. The particle size is always less than 2 mm [43].

Therefore, four types of copper waste to be reviewed can be established: (I) tailings with sizes smaller than 1 mm and with large amounts of contaminants, (II) smelter slags smaller than 5 mm with contaminants to a lesser degree than the previous one, (III) smelting or roasting ashes and powders with sizes smaller than 2 mm and typically smaller than 70 microns. (IV) neutralization cakes formed mainly by gypsum and metallic oxyhydroxides as a result of the treatment of acid currents. The latter usually have sizes greater than several cm, but once in contact with water and in the mixer, they behave like a granular material.

3. Definitions and Requirements of Concretes and Mortars

The definition in Europe of construction products and their characteristics is given by regulations. Specifically, by EN 206 for concrete [44] and EN 998-1 or EN 998-2 for mortars depending on their application [45,46].

Concretes are made up of cement, fine and coarse aggregate, admixtures, additives, fibers, and steel bars or meshes. The last three are far from the scope of this study because they are structural materials with high requirements. The mortars have the same composition than concretes, but without coarse aggregate and, furthermore, the proportions are not the same.

The role of cement in both products is fundamental since it is the material that acts as a binder. However, while the cement in concrete must meet certain requirements under EN 197-1 [47] for mortars there are no such requirements. This standard perfectly defines the components of cement and for years already includes some type of residue or by-product as a replacement for clinker: slag coming from iron processing and fly ashes coming from thermal centrals fed with coal.

In case of aggregates, it happens in the same way: aggregates in concrete applications must comply with the regulations given in EN 12620 [48], while in mortar applications in general it is enough to declare the aggregate grain size. This standard establishes requirements at three levels: geometric, physical, and chemical.

In the first requirement, the particle size distribution is determinant. In general, the regulation differences fine aggregates (0–4 mm) and coarse aggregates (>4 mm), but there are also requirements regarding their distribution (Table 1):

Table 1. Particle size distribution requirements for concrete manufacturing.

	Size	2D ¹	1.4D	D	d	d/2
Coarse aggregate	D/d < 2 or D < 11.2	100	98–100	85–99	0–20	0–5
	D/d > 2 or D > 11.2	100	98–100	85–99	0–20	0–5
Fine aggregate	D < 4 mm and d = 0	100	95–100	90–99	-	-
	Mixed	D < 45 mm and d = 0	100	98–100	85–99	-

¹ Where “D” is the largest particle size and “d” the lowest.

The physical requirements are important, but not decisive to discard the use of the waste as aggregate. This depends on its final application. However, it is noteworthy that the composition of recycled aggregates is measured visually, differentiating between concrete, aggregate, baked clay, asphalt, glass, and others.

The same is true for chemical requirements. They are not decisive to discard the use of a mining waste as aggregate, since this will depend on the final application.

Additions in the manufacture of concrete are more regulated, while for mortars there is freedom of use. In the first case, the additions can be certain residues (fly ash, silica fume, or granular slags) that cannot be modified or they can be pigments or fines for which there are no requirements other than those set by the manufacturer itself, although the recommendation is to usually limit them to 3% because these materials can be similar to the mineral filler.

Finally, the environmental aspect deserves separate consideration. Many of these wastes contain potentially dangerous elements such as As, Ba, Cd, or Hg and their application is limited by the values they present in leaching [49] (Table 2). In Europe, the values defined by the waste dumping regulations are taken as a reference and it is established that if it does not exceed the limitation imposed for inert waste, there should be no contamination.

Table 2. Leaching limits for inert residues.

Component	Leaching Test (L/S = 10 L/kg) (mg/kg Dry Matter)	Percolation (mg/L)
As	0.5	0.06
Ba	20	4
Cd	0.04	0.02
Cr total	0.5	0.1
Cu	2	0.6
Hg	0.01	0.002
Mo	0.5	0.2
Ni	0.4	0.12
Pb	0.5	0.15
Sb	0.06	0.1
Se	0.1	0.04
Zn	4	1.2
Chlorides	800	460
Fluorides	10	2.5
Sulphates	1000	1500
Phenol index	1	0.3
DOC ¹	500	160
TDS ²	4000	

¹ Dissolved Organic Carbon. ² Total Dissolved Solids.

Therefore, according to European regulations, copper mining waste has the potential to replace part of the cement and act as a hydraulic binder, either as an aggregate or as an addition. In mortars, there is freedom to add copper residues in any aspect, but in concrete

certain limits in terms of particle size distribution must be respected. In both cases, its application will depend on the leaching values.

On the other hand, obviously the use of these materials depends on the particular application that is regulated by the regulations of each country or even region. However, this is far from the purpose of this study. Here, it is intended to show the possibilities for the manufacture of materials. Its potential application will depend on each area.

4. Discussion: Issues and Possible Solutions

4.1. Cement

In general terms, copper waste has not been as widely studied as cement addition or other wastes from other industries (blast furnace slag, fly ash, or silica fume). This is because the composition of copper residues is not prone to improve the characteristics of the final products and also due to the contaminants within the residue that are not quantitative predominant but qualitative. Elements such as As, Hg, or Pb may add a hazardous characteristic to the new product. In fact, the mixture of these residues with cement has been applied as a fixation method in hazardous wastes [50–57].

In case of concrete manufacturing, mining and industrial copper waste is not included as allowed addition into cements, so their use is forbidden in the EU.

The potential uses of the copper residues in mortars manufacturing are higher than in concrete manufacturing. The cement additions should be limited by technical issues or requirements (mechanical behavior, durability, and toxicity) but not by the standards.

In general, the additions with high quantities of calcium (CaO) or silica (SiO₂) are positives. Calcium has hydraulic properties so its addition does not damage the mechanical properties of the final product. The silica behavior is more complex and it is related with pozzolanic activity. The silica must be reactive, meaning the silica must be able to form new chemical compounds with the cement, reaching a better resistance in the long term. This reactivity of the silica is related with the stability of the formed compounds: as higher stability of the compound (such as quartz), less reactivity will be presented.

Tailings may include high amounts of silica, but usually as silicates. Reactive silica is added to cement with the aim to reach calcium silicates thanks to the cement hydration reactions. However, the addition of these silicates before cement hydration will not provide better properties.

The slags from copper smelters consists mainly on ferric silicate, which can be used as pozzolanic if the silica is reactive. This depends on the silica composition, but can be activated through a thermic treatment. The limitation here is due to the costs of the thermic treatment and the advantages should be many to justify the price. In any case, the cement substitution by slags or tailings will be lower than 20%.

The addition of ashes coming from roasting in the cement manufacturing is not considered because the ashes content of metallic oxides and sulphur are detrimental to the properties of the final material. Neutralization cakes have a very high amounts of calcium but as gypsum which usually affects to the durability of the final product. However, it can be added in low quantities (5%) as setting regulator instead of natural gypsum. The substitutions of cement have been studied more in concrete manufacturing than in mortar manufacturing. Tailings with high amounts of silica (>75%) and low amounts of calcium (<10%) were mixed with cements in low proportions (<5%) obtaining good values, 42.5 N (compressive strength) [58]. Others tailings and two different neutralization cakes with low content in silica (28, 11, and 15% respectively) and calcium (25, 55, and 43% respectively) were used in low proportions mixed with other wastes to obtain a mix with a content of 13–14% of silica and 41–42% of calcium [59]. The results show how it can be an alternative if the mix is burned with the clinker. Other different wastes with silica (11.2%) and iron (85.3%) were added to a concrete (5–10%), obtaining better mechanical strengths [19].

On the other hand, the leaching behavior of the copper tailings has been assessed. The leaching value of the As is important because it is the main contaminant (due to their mobility and abundance), although others elements can also affect it. Cement addition is a

good technique to fix As so the substitution of cement by wastes in cement-based products is a convenient application. Very good results (in terms of leaching) have been achieved with substitution of 50 [50], 16 [54], 10 [55], 32, or 53% [56] of cement by wastes with high amount of As (1–32%).

Based on the bibliography, low grade substitutions of tailings or slags by cement in mortars are feasible. Although the properties may be lower, the cement process will be cheaper. Sulphur and contaminant addition should be limited.

The copper residues should be treated before recycling. Depending on the copper residue, a milling process can be required to obtain a particle size lower than 70 μm . Slags are a very resistant material, which may cause an increment in the costs. Tailings are much easier to mill, but the drying process may be required.

4.2. Aggregates

Most copper residues have fine or very fine particle size, so it is not easy to use them as coarse aggregates. Only slags may be used if they are mixed with natural aggregates (or other recycled aggregate) in order to obtain the appropriate particle size distribution. Neutralization cakes can be used as coarse aggregate applying just a simple crushing treatment, but due to their nature the particles have a very low resistance (gypsum) to be part of a concrete. In addition, the final product will have durability issues due to the sulphur content. So, it is recommended not to use copper waste as coarse aggregates.

For fine aggregates there is more flexibility. Only concretes have particle size requirements and they can be reached in a simple way. However, fillers (<80 μm) negatively affect the solidification so they should be limited to 3%. As has already explained, neutralization cakes are not good aggregates, so the application limit should be 1.5% for concrete manufacturing and 5% for mortar manufacturing.

Tailings with medium–high grain size and slags may require a crushing and sieving treatment to obtain fine aggregates. For the residues' application in concrete manufacturing there are some requirements about the distribution, but for mortar manufacturing more flexibility is accepted. As orientation, the standard sand has a maximum size (D) of 2 mm meanwhile other very common D are 4 mm, which is the recommended grain size for aggregates application.

Figure 2 shows the particle size distribution of the normalized sand used in mortars manufacturing and the acceptable limits for the concrete manufacturing. This size distribution is not necessarily the most appropriate to obtain the best results, but just a reference understanding that very high deviations will negatively affect the final product anyway.

The use of aggregates with sulphur (with similar composition than copper tailings) to substitute both coarse and fine aggregates in concrete manufacturing has been studied [13]. Compressive strength shows that complete substitutions provide competitive results compared with the standard products. Slags have been also studied as a substitution of the fine fraction [8] of the aggregates. For substitutions up to 80%, the compressive strength obtained is the same as the one presented in the standard materials. In mortars with complete substitution, slags provide better properties than natural sand [9].

On the other hand, the environmental aspect of the aggregates manufactured with copper residues is relevant because all copper wastes would leach and their use will be restricted (except slags, which are stables). Consequently, copper wastes provide better alternatives if they are used in cement-based materials and commercialized as final products: concrete and/or mortar. These final products will be marketable, if the suitability, non-toxicity, and stability of the final products are demonstrated within detailed leaching studies. This is the key concept to reuse copper wastes as aggregates: to market the final products.

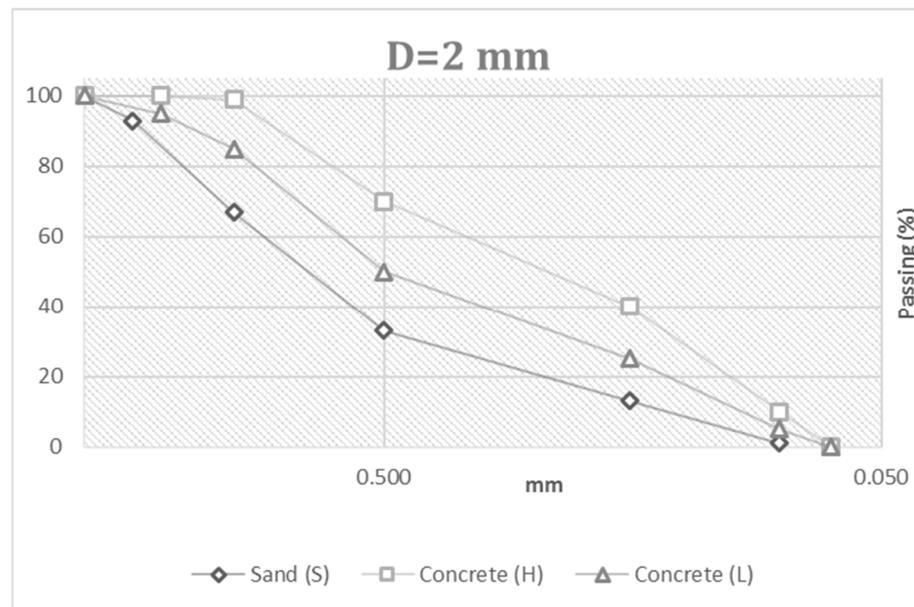


Figure 2. Particle size distribution of normalized sand, and the high and low limits for concrete.

In the previous section, the fixation of the toxic elements have discussed. In the aggregates case, the situation is similar: cement contributes positively to reducing the hazard of wastes. However, it should be considered that the total amount of arsenic in the cement-aggregates mixtures will be higher due to the greater proportion of aggregates than cement both in the manufacture of mortars and in the manufacture of concrete. Although there are some positive results such as the slags without leaching behavior, even long-term results, there is still a need to evaluate each final product designed.

5. Conclusions

The main conclusion is that the possibilities of adding copper residues (Figure 3) are more restricted in concrete manufacturing than in mortars manufacturing and the use of mortars is also restricted (it is not possible to make pieces with mortar such as curbs or pavers). Copper waste is suitable to be used as a substitute for cement only for mortars for manufacturing. As substitute of fine aggregates, they can be used in both mortars and concrete (with some restrictions). The application should be in final products instead of aggregates.

Tailings and slags can be used as cement addition or as aggregate depending of the particle size and the crushing treatment. If particle size is lower than 80 μm , the use in cement (<20%) is recommended instead of in aggregates (<3%). If the particle size is higher, the suggestion is to use fine aggregates in concrete and mortars. Slags are especially good as aggregates due to their resistance.

Ashes has lower uses. In cement, they will not provide improvements, but can be used in mortars (<20%) with the aim of obtaining a cheaper product. As filler in fine aggregate, it is not recommended, but it can be used (<3%).

Neutralization cakes can be a good option as solidification regulator (<5%) instead of natural gypsum. This is a better option than substitution of aggregates for concrete (<1.5%) or mortar manufacturing (<5%).

In all cases, the leaching behavior should be studied. Several technics can be applied in the case of hazardous elements presence out of the limits, but the easiest solution is to limit the waste proportion to be added in the final product.

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