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CEReS – Co-processing of Coal Mine & Electronic Wastes: Novel Resources for a Sustainable Future

C.G. Bryan^{1,2*}, B.J. Williamson², J. Calus-Moszek³, Q. van Haute⁴, A.-G. Guezennec¹, S. Gaydardzhiev⁵, P. Wavrer⁶ and R. Frączek⁷

¹Water, Environment & Ecotechnologies Division, BRGM, Orléans, France. ²Camborne School of Mines & Environment and Sustainability Institute, University of Exeter, UK. ³Central Mining Institute, Poland. ⁴Comet Traitements SA, Obourg, Belgium. ⁵Laboratory of Mineral Processing and Recycling, University of Liège, Belgium. ⁶CASPEO, Orléans, France. ⁷Geology and Mining Surveying Department, TAURON Wydobycie SA, Poland.

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*Correspondence: c.bryan@brgm.fr (C.G. Bryan).

Abstract: Most coal mines produce waste which has the potential to generate acid mine drainage (AMD). If not properly managed, this can cause environmental damage through contamination of ground and surface waters and soils for hundreds of years. At the same time, the pace of technological development means that most electrical and electronic equipment becomes obsolete within a matter of years, resulting in the generation of vast quantities of electronic waste (e-waste). Where this cannot be recycled, it must be discarded. The CEReS concept is a co-processing approach for both waste streams to produce metals and other valuable products, and to reduce or eliminate their environmental impact. This brings together two waste streams from opposite ends of the supply chain; turning each into a novel resource in a single, coherent ‘grave-to-cradle’ process. This industrial ecology approach is key to supporting a circular economy whilst securing the sustainable supply of critical raw materials. The project successfully elaborated a novel co-processing flow-sheet comprising: (i) the accelerated bioweathering of AMD-generating coal production wastes to generate a biolixiviant; (ii) the pyrolysis and catalytic cracking of low-grade PCBs to produce hydrocarbon fuel, a halogen brine and a Cu-rich char; (iii) the leaching of base metals from the char using the biolixiviant; (iv) the reuse of stabilised coal wastes; and (v) the full or partial (as enriched substrates) recovery of valuable metals. These process units were demonstrated individually at lab-pilot scale.

The data were then used to validate the entire flow-sheet in an integrated process simulator and determine the economic balance. Finally, an LCA approach was used to demonstrate the environmental benefits of the CERE_S process over the status quo.

Keywords: AMD, Electronic Waste, Mine Waste, Pyrite, Co-processing, Industrial Ecology

1. Introduction

The European Union's urgent need for increased job creation, economic growth and resource independence is seemingly juxtaposed with its commitments to environmental rehabilitation and protection. Environmentally sustainable economic growth as a reality requires the development and implementation of innovative solutions to primary resource shortages and waste management.

CEReS was a project funded by the Research Fund for Coal and Steel (RFCS) to develop a co-processing solution for the treatment of acid-generating coal mine wastes and the recovery of (critical) raw materials from electronic wastes. Poland was chosen as a case study region, largely due to its substantial coal mining industry, challenges with subsequent wastes and relatively underdeveloped e-waste recycling sector. The project set out to demonstrate the technical feasibility of the individual unit processes at laboratory/pilot scale. These were then integrated *in silico*, and an economic assessment made. A life cycle assessment (LCA) approach was used to evaluate the environmental benefits of the CEReS process compared with the business-as-usual, "do-nothing" scenario.

1.1. Coal Production Wastes and the Environment

Europe hosts large and growing volumes of wastes from past and present mining activities, of which coal production is the greatest single contributor. At the turn of the millennium, coal wastes accounted for some 2.4 Gt of the 5.9 Gt total mine wastes and tailings stockpiled within the EU (Charbonnier, 2001; Lottermoser, 2010). Since 2008, Europe has produced on average over 500 Mt solid fossil fuels *pa*, of which approximately 20% was hard coal (Eurostat, 2020). Poland is Europe's largest producer of hard coal with 31 active coal mines, producing an average 74 Mt hard coal (declining from nearly 84 Mt *pa* in 2008 to just over 63 Mt *pa* in 2018; Eurostat, 2020) and ~30 Mt waste *pa* (Szczepańska-Plewa et al., 2010).

Coal mining waste is produced at all stages of mine development and deposit exploitation, from shaft sinking to making rock drifts in deposits, but the vast majority (almost 95%) of the waste produced is mineral processing waste (coarse-grained, fine-grained and flotation waste as well as sludge from sludge-water circulation systems). Hard coal mining is one of the biggest producers of industrial waste in Poland, accounting for 25-30% of annual industrial waste production (GUS, 2018). Currently about 90% is used in geoengineering while the rest is deposited in the environment, with well over 600 Mt currently stockpiled (Szczepańska-Plewa et al., 2010). This has mainly been stored in heaps,

which has resulted in increased costs of hard coal production and permanent adverse changes to the natural environment. The Polish Act on Mining Waste¹ states that this waste should be recovered at the site of its production. Therefore, the management of hard coal mining and production wastes is a legal, environmental and economic challenge for the industry.

1.1.1. Environmental Impact

Coals come from reducing environments and as such, they commonly contain iron sulfides such as pyrite. During coal beneficiation these sulfide fractions, if present, report to the wastes. Where such wastes are exposed to oxygen and moisture, the microbially-mediated decomposition of the pyrite and other sulfide minerals can cause the formation of acid mine drainage (AMD). AMD is characterised by low pH and varies widely in composition, with elevated concentration of sulfates, iron, manganese, aluminium, other toxic and radioactive ions as well as excessive total dissolved solids common in AMD from sulfidic coal wastes.

AMD from underground and surface mines, waste dumps and tailing dams is one of the oldest and most consistent industrial problems facing mining regions in Europe and elsewhere, affecting at least 5000 Km of Europe's rivers (Jarvis and Younger, 2000; Lottermoser, 2010). The impact of acid mine drainage is primarily on the receiving watercourses, where its effects are complex. It is a multi-factor pollutant, and affects ecosystems through a number of direct and indirect interactions that can be both chemical and physical (e.g. Gray, 1997). Chemical effects are the result of pH, dissolved solutes and salinity, whereas physical effects are caused by the precipitation of secondary minerals and metal oxides. AMD will affect different ecosystems in different ways, and it is difficult to distinguish which component will have what effect, or which, if any, may be more important.

The longevity of AMD genesis is one of the key aspects to the problem. Unlike other industries where cessation of operations will lead to a significant reduction in pollution, the reverse is often true for the mining industry. Uncontrolled oxidative dissolution of exposed sulfide minerals will lead to continuing pollution on a time scale often greater than the entire life of the mine.

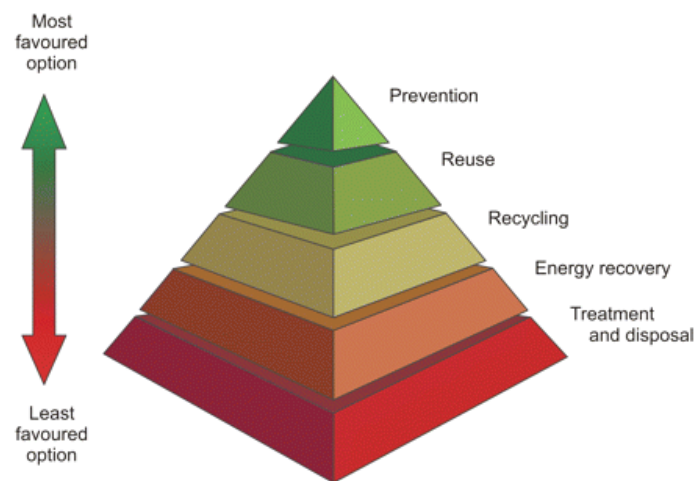
1.1.2. Management of Acidogenic Coal Production Wastes

A mine waste hierarchy; the order in preference for mine waste management strategies, is shown in Figure 1. The prevention of waste production is unachievable; therefore, reuse and recycling are the most-favoured, viable options. The most common options for the reuse of coal production wastes

¹ Journal of Laws No. 138, item 865, with later amendments

include: (i) backfill for open voids; (ii) landscaping material and revegetation substrate at mine sites; (iii) aggregate for civil engineering projects; and (iv) feedstock for cement and concrete.

However, the presence of sulfides causes geotechnical stability as well environmental problems as a result of their decomposition. This unstable sulfide content renders such wastes unsuitable for use in civil engineering projects or backfill/landscaping of the mine, limiting the possibilities to reuse or recycle many coal production wastes. (Significant impacts from the reuse of sulfide-bearing coal wastes in civil engineering projects are not uncommon, e.g. the Buków flood polder, ground levelling and backfilling; Stefaniak and Twardowska, 2010; Szczepańska-Plewa et al., 2010). Therefore, the majority of (acidogenic) mine wastes produced at mine sites are still placed into storage facilities



(Lottermoser, 2011).

Figure 1. The mine waste hierarchy (Lottermoser, 2011).

Current BAT (best available techniques) for managing acidogenic coal wastes and residues is to prevent seepage from waste dumps and dewater tailings (EC, 2009; Verburg et al., 2009): covering them with appropriate materials (composite/vegetative/wet covers, etc.) in order to prevent moisture and oxygen ingress, thus preventing AMD formation or to store pyritic material below the water table. This solution is costly and does not address the issue of AMD generating potential. The capping materials have a limited lifetime, and constant monitoring is required. Should the material be (re-)exposed to oxygen and moisture, microbial weathering and thus AMD generation will (re)commence. With increasingly extreme weather events more likely as a result of climactic changes and increasing pressure to reuse brownfield sites, the disturbance of apparently stable mine waste impoundments seems certain.

The environmental consequences of poorly managed or improperly stabilised waste piles are well documented and greater effort needs to be made to provide reuse and recycling options that are environmentally sound. Clearly, a major step required to enable alternative options for acidogenic waste use is therefore the removal of labile sulfide content (Kazadi Mbamba et al., 2012).

1.1.3. Biomining sulfidic mine wastes

Biohydrometallurgy (or biomining) is a credible biotechnology used in the mining industry. It exploits the actions of lithotrophic microorganisms to recover metal from their ores. These organisms get their energy from the oxidation of iron and/or reduced inorganic sulfur compounds (RISCs), producing sulfuric acid and ferric iron. Ferric iron (Fe^{3+}) is the primary oxidizing agent, attacking sulfide minerals (MS), as seen in Equation 1, and the role of the organisms is the regeneration of Fe^{3+} from Fe^{2+} and the oxidation of sulfur compounds to produce sulfuric acid (Equations 2 and 3).



The result is a highly corrosive “biolixiviant” solution which attacks the mineral matrix in which target metals are entrained or form an integral part (for example copper from chalcocite or gold entrained within arsenopyrites).

Biomining was successfully used in the re-processing of sulfidic mine wastes at the Kasese Cobalt Company site in Uganda where cobalt was produced from old copper mining tailings (Morin and d'Hugues, 2007). By contributing to the stabilisation of those wastes, this biohydrometallurgical operation has also drastically decreased the AMD discharge in the environment. While this can be applied to mine wastes with an economically viable grade of valuable metals, in many cases the value of the metals within AMD-producing wastes is not sufficient to cover the costs of reprocessing them directly. This is especially the case when considering pyritic coal production wastes, which do not normally come from valuable metal-bearing assemblages.

Studies since the 1960's have shown bioleaching can effectively remove inorganic and organic sulfur in coal prior to combustion (Cardona and Márquez, 2009; He et al., 2012; Hoffmann et al., 1981; Olson and Kelly, 1991; Schippers et al., 1999). Up to now this is not done commercially, despite the design and operation of pilot scale systems to remove both pyrite and organic sulfur (Cara et al., 2005; Milan et al., 2017; Ors et al., 1991; Rossi, 2014). Again, such approaches were designed for the removal of sulfur from coal, not coal production wastes. Such an approach uniquely for

desulfurisation of waste is difficult to justify financially over preventative methods: once the sulfide is leached, there is a need to spend extra money on neutralisation of acid and management of iron (Klein, 1998). Conversely, in the CEReS process, the acid and ferric iron is a desirable product. CEReS uses biodesulfurisation to remove pyrite (and other sulfides/metals) from coal production wastes, and makes use of acid and ferric iron generated (as a biolixiviant), rather than requiring immediate neutralisation.

1.2. Electronic Wastes

Supplying and securing mineral resources with minimum environmental footprint is a serious challenge, especially for the European Union which consumes 25 to 30% of the world's metal but accounts for around 5% of the world's mining output (Östensson, 2006). European dependency on metal import is growing every year despite efforts in the development of recycling technologies and material science. This has been further emphasised in the "Criticality Report" compiled for the European Commission in 2010 and revised in 2014², in which 20 mineral raw materials have been explicitly named as highly critical for the industrial development and economic security of the European Union. These tensions highlight the need to associate the identification of new potential resources that could be used for the recovery of rare and valuable materials with the development of recycling processes in order to close the gap in raw materials. Improving their mode of production and developing a circular component of the economy is imperative.

Among the different types of secondary post-consumption wastes, electronic-wastes (e-wastes) represent the fastest growing and most problematic waste stream in the world. In the EU, 10-12 million tonnes are produced *pa* (Balde et al., 2015; Goodship et al., 2019; Huisman et al., 2008). The Commission seeks to address this through DIRECTIVE 2012/19/EU on waste electrical and electronic equipment (WEEE).

1.2.1. Environmental Impacts

E-wastes contain a wide range of different metals and other compounds, many of which are highly toxic to the environment and human health. For example, a UK study has found that the presence of e-wastes in municipal waste is the major single source of toxic elements in the potentially biodegradable fraction (Papadimitriou et al., 2008). In Japan, more than half of the copper from WEEE ends up in landfill or is lost (Oguchi et al., 2012). EEE is made up of many individual components. These include printed circuit boards (PCBs), cathode ray tubes (CRTs; from older PC

² <http://ec.europa.eu/DocsRoom/documents/10010/attachments/1/translations/en/renditions/native>

monitors and TVs), batteries, internal and external wiring and the equipment casing. Each has its own unique composition and associated environmental hazards. Unsurprisingly, the Basel Convention has identified e-waste as toxic. As a direct result, e-wastes can only be exported where it can be shown that the wastes will be managed in an environmentally sound manner in the country of import. Despite this, and despite improving efforts to collect and recycle e-waste within the EU, significant amounts find their way to non-developed nations (Breivik et al., 2014), and the severe environmental implications of their improper storage and processing are well documented (e.g. Nnorom and Osibanjo, 2008).

1.2.2. Urban Mining

The majority of the value in e-waste is in the PCBs. On average 90% of the intrinsic economic value of PCBs is in the precious metals that they contain (Cui and Zhang, 2008; Luda, 2011). These metals make up the majority of the economic value of WEEE, and are in concentrations at least 10 times higher than their typical mineral ores (Huang et al., 2009; Tuncuk et al., 2012). Many of these are of significant strategic importance and are reaching their extraction peaks. The average price of rare earth ores has almost doubled since 2007 (Kingsnorth, 2011). China supplies 95% of the world's rare earths, and a recent 40% reduction in Chinese export quotas demonstrated the strategic importance of a reliable and secure source of rare earths. Nevertheless, China produces 90% of the world's electronic goods (Widmer et al., 2005). This is an 'open loop' in that it can be viewed as a net export of valuable raw materials.

The US Environmental Protection Agency has identified e-wastes as a good way of generating a source of valuable metals, in what it terms "Urban Mining" (EPA, 2011). Recovering metals from e-waste is potentially more energy efficient than mining raw material. For example, recycling metals directly can lead to huge energy savings: 95% for aluminium, 85% for copper, 65% for lead and 60% for zinc (Cui and Forssberg, 2003; Nnorom and Osibanjo, 2008). Therefore, it is desirable to reprocess e-wastes not just on environmental grounds, but also economic.

1.2.3. Current WEEE and E-waste Processing Options

The best options for dealing with WEEE and e-waste are direct reuse and resale or remanufacturing via refurbishment (Cui and Zhang, 2008). However, given the short lifespan of many electronic devices, particularly computers and mobile phones, this is not always achievable as a major destination. Landfill is the least desirable option, and most countries are increasingly limiting this due to land contamination issues and associated cost of toxic compound handling and disposal. Therefore, recycling is the most pragmatic approach for value recovery and environmental protection (Lundstedt, 2011).

PCBs are a mixture of polymers, ceramics and metals tightly bonded together. The board itself is made up of fibreglass-reinforced thermosetting matrix, which may contain up to 15% bromine (used in bromo-phenol flame-retardants; Luda, 2011). They are among the most complex sub-components of e-waste and most difficult to reprocess. The metal content of the PCBs is highly variable, depending on the type and make of the equipment. The metal content determines process selection and economics. For example, PCBs from mobile phones tend to contain greater concentrations of metals than those from PCs, while boards from TVs contain less than 100 ppm gold are usually considered low-grade (Kasper et al., 2011).

Pyrometallurgy is the traditional choice for metal refining from processed (usually upgraded) e-waste, resulting in the production of precious metal-bearing copper bullion (Tuncuk et al., 2012). This means that selective recovery of individual metals is effectively impossible by this route, and further recovery processes are needed. It can be done within existing smelters treating mineral concentrates, where e-waste may be combined (10-15%) with a copper concentrate (Cui and Zhang, 2008). However, it is energy intensive and requires a relatively high grade feed material, and the ceramics contribute to final slag volume. Proper emissions control is also necessary due to the production of dioxins, furans and other polybrominated organic compounds and polyaromatic hydrocarbons during PCB incineration (Huang et al., 2009).

Well-regulated smelters have processed 15-20 thousand tonnes of e-waste with 95% metal recovery and minimal generation of dioxins, though the economic viability is often questionable; reports indicate that the cost of smelting PCBs approximately equates to 50% of the revenue generated (Lehner, 1998; Mark and Lehner, 2000; PHA, 2006).

At present within the EU there are only three dedicated smelters (the Umicore plant in Hoboken, Belgium, the Rönnskär Smelter in Sweden and the Kayser Recycling Smelter in Aurubis, Germany) that can handle e-wastes (Khaliq et al., 2014). A requirement however for the PCB's to enter as input streams in these installations is that precious metals concentration should exceed a given cut-off grade. Given the disparate nature of e-waste production, there are logistical limitations to collection and transport. Moreover, in such a process critical metals such as REE are lost to the final slag, and there is limited or no recovery of other products such as halogens or fuels. Thus, there is still significant waste in the system and loss of valuable resources as a result.

Compared to pyrometallurgy, hydrometallurgical processes offer relatively low capital cost and are particularly suitable for small-scale installations (Tuncuk et al., 2012). An added advantage is their flexibility, offering a possibility for selective extraction of base and precious metals of interest in e-waste and PCBs. Since major metals exist in their elemental or alloy form in PCBs, their

hydrometallurgical extraction has been tested using various oxidants (lixiviants; hydrogen peroxide, oxygen, ferric iron, etc.) under acidic (HCl, H₂SO₄, HNO₃ etc.) or ammoniacal and chloride leaching environments. While cyanide is the most economically feasible of common leaching methods, it is also the highest in terms of toxicity. Research and development in hydrometallurgical applications remains rather scattered and mostly at lab-scale. Therefore, the generation of operational and cost data via pilot scale tests is essential. Moreover, the costs of the lixiviants contribute to overall operating expenditure of hydrometallurgical options which may include treatment of heavily polluted by-products in special waste disposal facilities, and further limits the grade of PCB that can be treated economically. Consequently, there are only a limited number of hydrometallurgy operations in Europe for e-wastes and these are reserved for high grade materials; there is currently no suitable option for low-grade PCBs and a lack of PCB processing capacity more generally.

1.2.4. Biomining electronic wastes

Studies into the bioleaching of e-waste have mainly involved the treatment of printed circuit boards (PCBs). The use of organic acids produced by various fungi or biogenic cyanide has been examined, particularly for the recovery of gold and other noble metals (Brandl et al., 2001; Brandl et al., 2008; Chi et al., 2011; Faramarzi et al., 2004). However, such approaches require the selective cultivation of specific microorganisms in *circum*-neutral media rich in organic substrates. This requires aseptic growth conditions and is unlikely to be practical (or economic) when treating large volumes of non-sterile e-wastes. Therefore, the use of ferric iron and/or proton lixiviants produced by extreme acidophiles is preferable. There is no need for sterile conditions, and media are simple, comprising key nutrients such as sources of nitrogen, potassium and phosphorus.

In one-step tests (where the e-waste and microorganisms are introduced in a single vessel), reported copper recovery efficiencies vary widely from less than 4% to 100% (Rivero-Hudec et al., 2009; Wang et al., 2009; Xiang et al., 2010; Zhu et al., 2011) with leaching times typically greater than 10 days and pulp densities around 1% or less. Performance decreases significantly with increasing pulp density (Brandl et al., 2001; Liang et al., 2010; Wang et al., 2009; Xiang et al., 2010; Zhu et al., 2011). Generally, the lower the initial pH, the better the performance, though optimal pH ranges are apparent below which the organisms suffer. The same is true of ferrous iron concentration; optimal performance is reported between 7 and 9 g L⁻¹. Above this, factors such as proton consumption during iron oxidation and ferric iron precipitation affect final metal recoveries (Choi et al., 2004; Xiang et al., 2010; Zhu et al., 2011). The waste tends to be acid-consuming, probably as a result of several factors including the dissolution of acid-soluble metals. Performance may be better where constant pH is maintained (Yang et al., 2009), but this is not universal (Vestola et al., 2010). Several

studies have demonstrated improved leaching performance in media containing elemental sulfur as well as ferrous iron (Ilyas et al., 2007; Liang et al., 2010; Wang et al., 2009).

The toxicity of the e-waste on the microorganisms has been shown to be the major problem preventing efficient leaching. Up to 90% copper recovery from a 10% pulp density within 18 days has been reported using a culture adapted to high metal concentrations (Ilyas et al., 2007). However, the crushed PCBs were pre-washed in saturated NaCl and contained relatively low levels of copper (8.5% w/w). Nevertheless, adaptation to elevated metal concentrations rather than prewashing the e-waste seems to be more important in improving leaching rates.

Staggering the production of the lixiviant and the addition of the e-waste in a two-step process has been shown to greatly increase final copper recoveries and leaching rates (Liang et al., 2010; Xiang et al., 2010; Yang et al., 2009; Zhu et al., 2011) but has not been tested at pulp densities greater than 2%. Furthermore, if the addition of the e-waste at the second step results in a loss of culture viability, then fresh media and inocula will be required for each subsequent run and it may not be possible to subculture from one run to the next.

In mineral bioleaching the source of iron and sulfur which is oxidised by the microbial community to produce the oxidising lixiviant solution is inherent in the form of pyrite or other sulfide minerals (it is an autocatalytic process). In the current e-waste bioleaching practices, this must be provided in addition to the nutritive medium. This is usually in the form of ferrous sulfate with acid provided directly via pH control with sulfuric acid or through the addition of elemental sulfur. Furthermore, PCBs are highly acid-consuming and require a high degree of pH modification to maintain an acidic environment necessary for the microbial action and maintained metal solubility. These chemicals adding increases the operating cost of the process.

While such lab-scale studies provide evidence that biohydrometallurgical reprocessing of e-wastes is technically possible, the wider economics of such a process are unlikely to be favourable with the current state-of-the-art. CEReS will decouple lixiviant production from PCB leaching in a two-step process to avoid issues of toxicity.

The lixiviant will be derived from a net acid generating source (sulfidic mine wastes) as opposed to ferrous sulfate (the oxidation of which is acid consuming; Equation 2) to overcome acid-consumption issues. Such an approach has been successfully demonstrated a varying scales of application to waste PCBs (Bryan et al., 2015; Guezennec et al., 2015) and other forms of post-consumer, metallic waste (Lewis et al., 2011). The use of biohydrometallurgy to generate the lixiviant from mine wastes is preferable to chemical oxidation options as it can be done at standard temperature and pressure, does not require expensive or environmentally damaging reagents and traditionally offers lower

operating expenditures as a result. In this context, CEReS concept can be seen to be simultaneously upgrading the metal content of mine wastes while providing a source of lixiviant to the e-waste making reprocessing economically viable both in terms of metal recovery but also operating expenditure.

2. CEReS

The co-processing approach proposed by CEReS employs AMD-generating coal production wastes as a cheap source of leaching solution (lixiviant) to recover metals from e-wastes. The novel flow-sheet will (i) remove the AMD-generating potential of coal wastes, ensuring their long term environmental stability while expanding avenues for their safe reuse; and (ii) enable selective recovery of base metals from waste PCBs, while concentrating precious and critical as well as rare earths into enriched substrates.

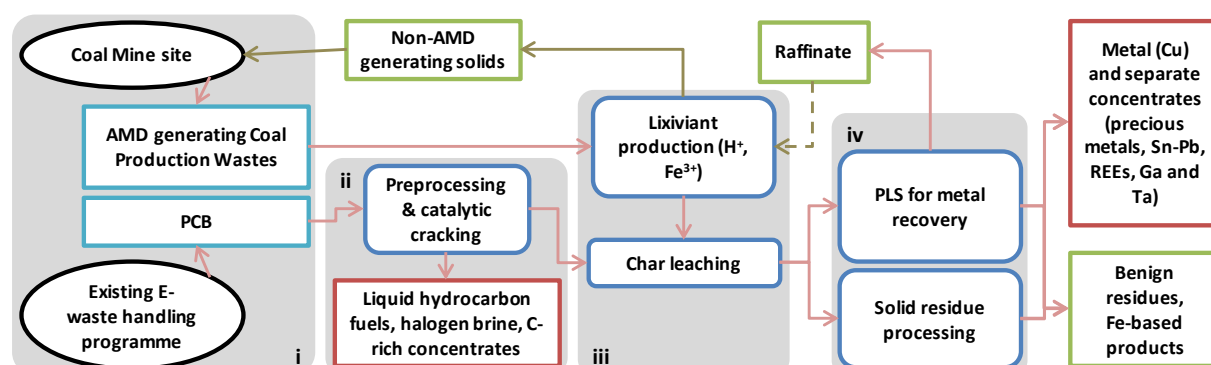


Figure 2: Simplified overview of the proposed CEReS co-processing flow-sheet.

The proposed CEReS process is an example of industrial ecology (Frosch, 1992). It brings together two waste streams from opposite ends of the supply chain, turning each into a novel resource in a single, coherent ‘grave-to-cradle’ process. The proposed co-processing concept is summarised in Figure 2, and can be considered in four parts:

- i. **Raw Materials.** AMD-generating coal mine wastes are recovered from existing mine waste dumps or during ongoing production. PCBs (shredded) are bled off from existing waste electronic and electrical equipment (WEEE) or e-waste handling streams. Therefore, there are no mining or comminution costs associated with the supply of raw materials for the CEReS process.
- ii. **Pyrolytic Cracking.** A catalytic cracking circuit is used for pre-treatment of the PCBs resulting in a metal-rich char. Catalytic cracking partially converts the organic fraction into a liquid fuel (which can be used for electricity generation) and a carbon-rich solid residue (with potential applications as a reducing agent in metallurgy or steelmaking). A quenching process removes

halogens (mostly bromine) as a saleable brine. The low temperatures and reducing conditions prevent the formation of dioxins while maximising product recovery.

- iii. **Lixiviant Production and Char Leaching.** A bioreactor system is used to oxidise sulfide minerals in the coal wastes (effectively accelerating AMD production), resulting in the production of a ferric iron-sulfuric acid lixiviant. This is used to leach base and other soluble metals from the PCB char. The stabilised coal wastes (depleted of their AMD-generating potential) can be used in the production of brick and ceramic elements or in civil engineering (aggregates) or, if they contain a high enough coal content, in feed for a coal-fired power station.
- iv. **Metals recovery and process residues.** Valuable metals (Cu and potentially REEs, Ga and Ta) are recovered from the pregnant leach solution (PLS) by an appropriate downstream process and the raffinate recycled to the coal waste bioleaching reactor. This circuit will include a system for managing the iron content, as significant amounts will be encountered throughout the process as a whole. Precious metals, lead and tin will report to, or remain in, the solid leach residue and will be physically separated to produce concentrates suitable for established refining metallurgy.

Thus, the fundamental idea behind CEReS lies in the observation that there is an excess of acidic effluents from coal wastes released in the environment (in the form of AMD) and a need for cheap, effective lixiviants in hydrometallurgical treatment of PCBs. Coupling both these fluxes in an intelligent manner will result from one side in a reduction in the environmental impacts of these wastes through the generation of benign residues, and from other side in the recovery of strategically important metals.

The exchange of wastes, by-products, and energy among closely situated companies is one of the distinctive aspects of industrial ecology. By organising the co-development of remediation and recycling technologies in very specific local context (proximity of post mining and urban waste collection/treatment sites) and by including a LCA approach in the project development, CEReS will demonstrate the applicability of an industrial ecology approach to both coal mining and recycling businesses. CEReS sought to deliver a practical, flexible, sustainable and profitable alternative to classical waste management systems for both coal and post-consumer wastes. CEReS will mainly target a waste flow (low grade PCBs) that is currently not treated by pyrometallurgy. Therefore, it is more a complement to, rather than in competition with, existing technical solutions (Figure 3).

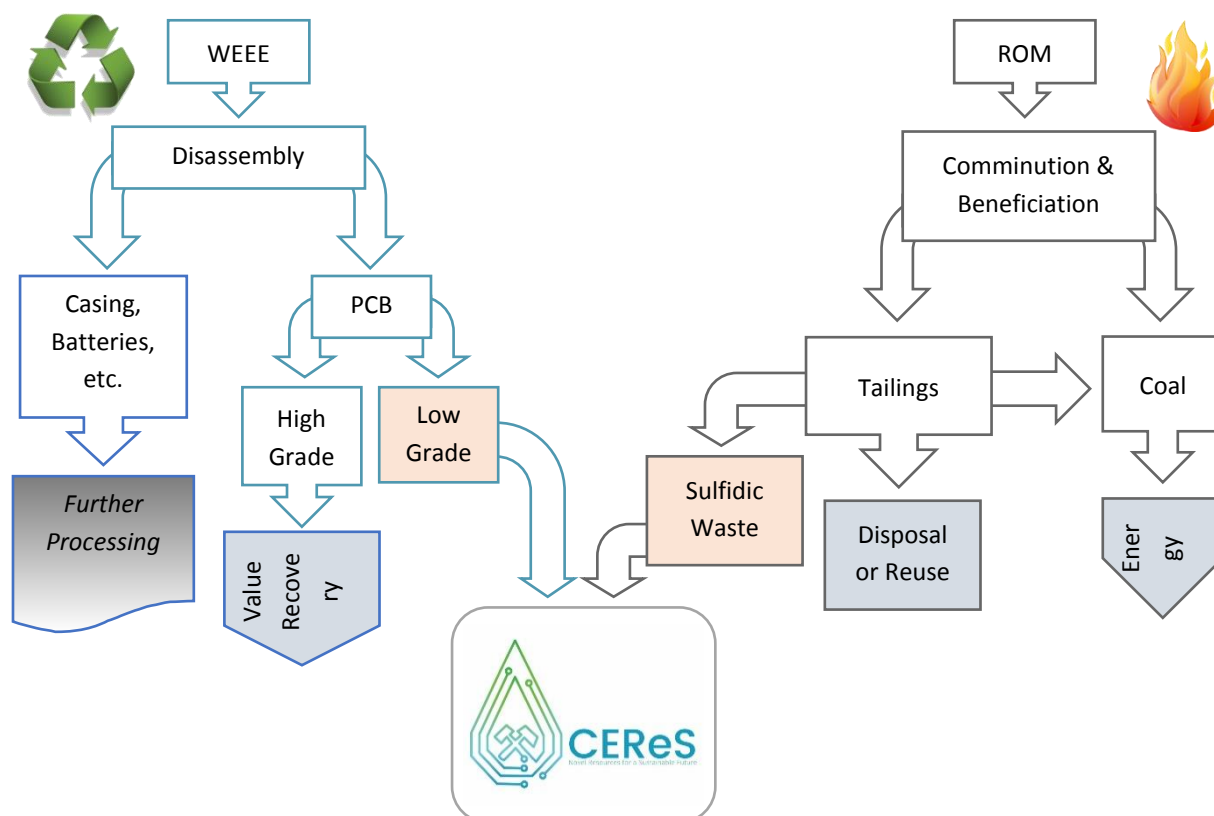


Figure 3. Industrial ecology of CEReS

To achieve the objectives the project was broken down into a series of interlinked work packages (WP). WP1 was used to obtain and characterise the raw materials required for development of the CEReS process as well as cross-mapping EU-wide occurrences of these wastes. The shredded PCBs cannot be leached effectively as they are, due to issues with acid consumption and relatively low metal concentrations (due to entrainment within bulk glass fibre-polymer matrix). The primary objective of WP2 was to develop and optimise a mechanical pre-treatment combined with catalytic cracking and concentration step for the PCBs from WP1.

The bioleaching process was developed in WP3, using the coal mine wastes from WP1 to produce the leaching solution (biolixiviant) and environmentally benign (stabilised) coal mine waste. A major element of the CEReS concept is the conversion of environmentally-damaging coal mine wastes into re-usable, stabilised material. Therefore, WP3 was further devoted to the development and testing of re-use options for the desulfurised coal waste (for example as granulated material for civil engineering or such for mine rehabilitation). WP4 developed a leaching process for the extraction of base and high-value metals contained in the char originating from the pyrolysis of PCB's (WP2) using the biolixiviant from WP3. WP4 also developed downstream processing options for valuable metal recovery from the leachate.

These research and technical development WPs provided baseline data for the development of a process simulator (model) for the CEReS flow-sheet in WP5. The results of the experimental tests performed in WP 2, 3 and 4 were used to validate and refine the model and to assess the technical and socio-economic feasibility of CEReS. In depth analysis of CEReS process sustainability (from a technical, economic and environmental point of view) was done including detailed life cycle analysis.

The overall outcomes of the project are described below.

3. Raw Materials

3.1. Coal production waste

In Poland, especially in the Upper Silesian Coal Basin, there are about 160 potential mine waste dump sites. Some of those possess potential risk for the generation of AMD (acid mine drainage) due to the large presence of pyrite. Tauron Wydobycie S.A. own the Brzeszcze, Janina & Sobieski coal mines, and all generate sulfidic wastes during coal production.

Four waste types were considered from two mines, Janina and Sobieski: sludge (<0.1 mm), spiral tails (0.1-2 mm), jig tails (2-20 mm) and heavy liquid tails (20-200 mm). The sludge and heavy liquid tails were discounted due to their low sulfide content and difficulty with handling (either too fine or too coarse). The jig and spiral tails from Janina (JJT and JST, respectively) and Sobieski (SJT and SST, respectively) were extensively characterised. Detailed mineralogical analysis necessitated the development of a novel QEMSCAN[®] protocol, as graphite could not be used in the sample preparation, and the automated analysis struggled to differentiate the coal from the resin (Bransgrove et al., 2018).

Ultimately, the Janina spiral tails were selected for the project due to their high pyrite content (approx. 12%). However, subsequent QEMSCAN[®] analysis indicated limited liberation of the pyrite (25-30%). Chemical and biokinetic AMD prediction tests confirmed that the selected material was acid-generating. However, far less acid was produced than expected given the amount of sulfide oxidised (in both AMD tests and bioleaching experiments); this “missing acid” has yet to be explained (Bransgrove et al., 2018).

Currently, the Janina coal production waste is stockpiled on site. Samples were collected from the waste heap at the Janina mine in late 2016. These were used for microbial enrichments. Attempts were made to extract DNA from these samples with little success, indicative of relatively low microbial cell numbers. However, in a more comprehensive sampling campaign, comparing geochemical observations with high throughput DNA (16S rRNA gene) analysis, a community

dominated by strains typical of metal-rich, low pH environments was identified (e.g. *Acidithiobacillus* spp., *Leptospirillum* spp., *Sulfobacillus* spp., etc..), with a large fraction typical of saline environments (e.g. *Acidihalobacter* spp.) (Fonti et al., 2019).

3.1.1. Scrap printed circuit boards

The Polish WEEE market was analysed, and three categories of scrap PCBs were identified: high-, medium- and low-grade. The low-grade material was selected, but analysis found it was in fact a mixture of PCBs (~35%) and other parts of WEEE (such as shredded casing and other bulk components). For the development of the project, COMET Traitements – the partner leading the development of the catalytic cracking step - used low-grade PCBs from their own stocks. This material was analogous to the scrap PCBs available on the Polish market. Detailed analysis showed that copper represented approximately 23% of the intrinsic PCB value while precious metals represented over 60%.

3.1.2. Cross-mapping

A database was created to cross-map the occurrence of suitable mine wastes (dumps and mining operations) with WEEE handling facilities. This allowed the identification of geographically-suitable potential locations for a CEReS process. The database also contains data on sulfur contents in waste from coal processing plants and enabled the visualisation of information on the potential processing of electronic waste in particular waste management plants.

Three zones of distances were determined for an example coal production waste heap, which is located near the Janina mine in Libiąż. In a zone within 150 km from a potential source of coal production waste there are 35 e-waste processing plants (60% of all plants); within 150 – 250 km there are 15 plants (26% of all plants); and within 250 – 350 km there are 13 plants (13.8% of all plants). From an operational point of view, there is a good degree of existing co-location of coal mine and electronic wastes in the target region.

4. Pyrolytic Cracking

The treatment and recovery sector for scrap metal, end-of-life vehicles (ELVs), and WEEE generates a large amount of waste shredder residues (SR). These residues offer an ideal opportunity to recover materials that have become highly significant both economically and environmentally. In addition to this the European Union has set ambitious recovery targets for these materials. For example, 95% of an ELV must be recycled by 2015.

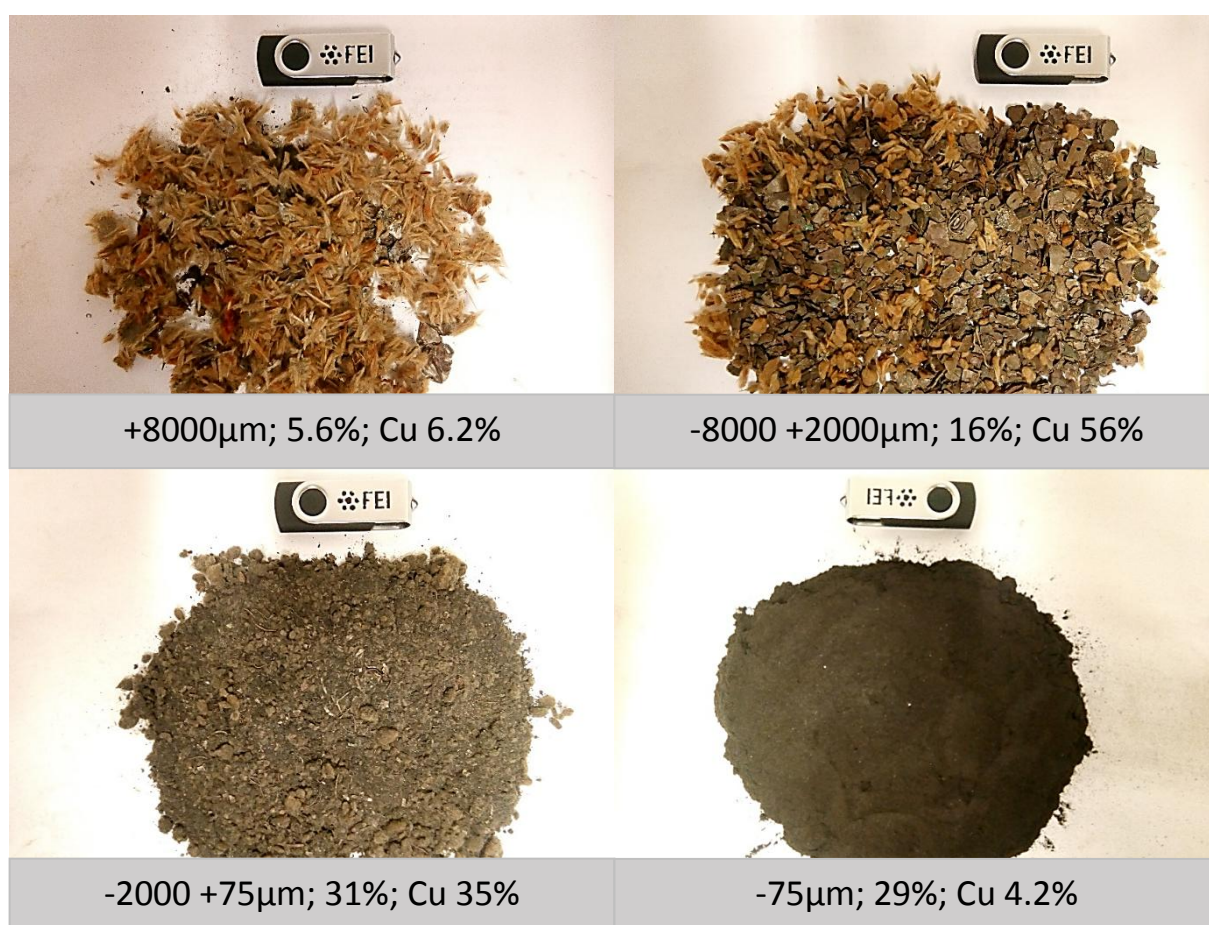
COMET Traitements SA developed and implemented new treatment and recovery processes that enabled the recovery of ferrous and non-ferrous metals, plastics, iron oxides and minerals from SRs. This work enabled COMET Traitements to achieve a recovery rate of 93.3%. Each additional percentage point represents significant R&D investment.

One of the main issues is the recovery of heterogeneous organic materials with a high calorific value, such as textiles, foams, plastic films, rubber and wood. COMET Traitements has already studied and evaluated the potential use of such materials in producing energy through treatments, such as pyrolysis and thermolysis. However, this research yielded negative results, including the production of dusty and tarry gases that had to be burned in-line, low yields of heat and possibly electricity and carbonaceous residues (char) that proved difficult to treat and recover (due to their high ash content, trapped or unburned heavy metals, etc). In light of these results, COMET Traitements has developed a process that allows polyolefins (PP/PE) to be converted into liquid hydrocarbons, which can then be used as fuel. This depolymerisation process uses a natural catalyst and co-reagents that allow for lower cracking temperatures and that target the recovered liquid hydrocarbons (C5 to C16). COMET Traitements have been developing this process for organic compounds that are more complex than polyolefins, namely materials found in SR such as mixed polymers, rubber, textiles, wood and foams. After recording promising results, COMET Traitements set up a pilot production unit at its site in Obourg.

An inherent characteristic of the metals in PCBs is that they are largely entrained within the ceramic and polymer matrix and pre-treatment is desirable to remove this material, liberate metal bearing components and improve their accessibility to leach solutions. CEReS transferred and further developed COMET Traitements' cracking technology to a dedicated PCB pre-treatment process for organics degradation and concomitant metal liberation and enables the recovery of additional value products. This cracking pre-treatment will allow three key innovations compared to the classical pyrometallurgical route: (i) an efficient management of the polymeric fraction leading to the production of high quality stockable liquid fuel and a carbon-based reducing agent; (ii) the recovery of the halogens (Br and Cl) as valuable brine or salt and (iii) the retention of elements such as rare earths, Ga and Ta in leachable forms in a polymetallic concentrate from which the different metals can be separated by hydrometallurgy.

Bench- and pilot-scale work at Comet successfully adapted the pyrolytic process to shredded scrap PCBs. Approximately 18% of the PCB mass could be converted to liquid and gaseous combustible hydrocarbons, the calorific value of which is sufficient to power the pyrolysis reactor at industrial scale, making the process energy-neutral. From labs tests, approximately 75% of the bromine

content of PCBs is released from the pyrolysis residue solids into the quench water, from which it is possible to produce a saleable Br product. A recovery method to extract bromine from the liquid hydrocarbon was tested which resulted in 69% removal of its bromine content. The metal-bearing char from the process was split into four size fractions (Figure 4): coarse (>8 mm, 6.2% Cu), mid (2-8 mm; 56 % Cu) fine (75 µm-2mm; 35% Cu) and very fine (<75 µm; 4.2% Cu). The mid fraction was sufficiently Cu, Au and Ag-rich that it can be sold directly to existing metal refiners. The very fine fraction can be disposed of conventionally while the remaining fractions are the target for char



leaching using the biolixiviant.

Figure 4. Char produced from the pyrolysis of shredded PCBs following attrition grinding. Percentages each fraction represents of the total mass are shown as well as Cu grade of each fraction.

5. Lixiviant Production and Char Leaching

5.1. Bioleaching and lixiviant production

Complete biooxidation of sulfidic minerals involves the action of a consortium of both iron- and sulfur-oxidising extremophile microorganisms adapted to an inorganic and acidic environment. Many

biomining microorganisms occurring naturally on mineral ores are known (Hallberg and Barrie Johnson, 2001; Rawlings and Johnson, 2007). Autotrophic species of the iron- and sulfur-oxidizing *Acidithiobacillus* genus and the iron-oxidizing *Leptospirillum* genus are significant contributors to commercial systems. Mixotrophic or heterotrophic acidophilic microorganisms such as *Sulfobacillus* spp., *Acidimicrobium* spp. and *Ferropasma* spp. are also important; not only for their contribution to mineral dissolution via iron and/or sulfur oxidation, but because they breakdown organic materials acutely toxic to the primary bioleaching organisms.

Initial work focused on the selection of an active and robust bioleaching microbial consortium through the adaptation of strains enriched directly from the wastes and/or consortia from other industrial and environmental locations. Bench-scale tests were done to establish empirical acid and ferric iron generation kinetic data. Given the fine nature of the mine wastes, a tank bioleaching system was preferable for the lixiviant production. The role of microbial adaptation and selection in improving process kinetics (with regard to stable production of an effective lixiviant from highly heterogeneous, low-grade material) was investigated and microbial evaluation and monitoring of reactors was undertaken.

Enrichment cultures were grown at 30, 42 and 48°C from samples from the Janina waste heap. Interestingly, an active bioleaching culture could not be obtained from the 42°C enrichment, theorised to be linked to the observation of low levels of *Leptospirillum ferriphilum* in the waste material. Two enrichment cultures at 30°C (TW30) and 48°C (TW48) were compared to two consortia of proven bioleaching ability: meso (30°C) and BRGM-KCC (42°C). Following extensive tests, the TW48 culture at 48°C was selected. Interestingly, there was a progressive loss of *Leptospirillum* spp. from 42°C tests (BRGM-KCC) during scale-up. The reasons for this could not be clearly explained (Fonti et al., 2019).

A biolixiviant could be produced from the coal production waste, containing approximately 10 g/L Fe^{3+} , and this was shown to be capable of leaching base metals from the char. Initial bench-scale tests showed greater than 80% removal of the pyrite within 5 days; kinetics that should be improved with further process optimisation and scale-up.

There was significant damage to the metallic components of the bioreactors at both lab and pilot scale. Subsequent investigation showed that the Janina coal waste contains significant amounts of salt, due in part to its geological setting (Herzig et al., 1986). Therefore, it is presumed that the reactor damage was caused by the chloride content of the waste. A simple washing step was shown to remove this salt and prevent subsequent corrosion. However, this would inevitably affect the economics of the process at a commercial scale. On the other hand, lab-scale tests have shown that

the Sobieski material is also amenable to bioleaching without the chloride issues, and so this may be considered as an alternative site in the future.

5.2. Char leaching.

The feasibility of the biolixiviant generated from coal wastes bioleaching as a leaching agent for extraction of the base and high-value metals contained in the char originating from the pyrolysis of PCB's was tested.

Two reactor designs were considered: a typical stirred-tank reactor (STR) and a rotating drum reactor (RDR). The RDR comprises a horizontal mesh drum containing the char, which rotates within a sealed outer drum containing the lixiviant/leachate. Various operating conditions and char pre-treatment options were tested. Finally, an attrition grinding pre-treatment followed by wet separation was used to prepare the char for leaching. The best performance was obtained with an STR set-up, but this was not suitable for the coarser (2-8 mm) char fraction. Conversely, the RDR was not suitable for leaching the finer fractions as the char was not retained within the inner mesh drum. Therefore, the RDR was selected to leach the coarse fraction and an STR for the fine fraction.

The leaching profile was bi-phasic, with a rapid initial dissolution of up to 40% of the copper over a few hours followed by a much slower phase (Arinanda et al., 2019). One possible explanation for this could be the formation of oxidised copper phases after the pyrolytic step (during quenching or attrition grinding, for example). However, it is more likely linked to the stoichiometric ratio of ferric iron to oxidisable metals. While there was some evidence of microbial colonisation of the char leaching reactor, the benefit of this to the process was not conclusively proven. Maintaining microbial activity (iron-oxidation) in the char leaching reactor could help overcome the stoichiometric limitations and lead to more efficient char leaching, and has been shown to be beneficial in other similar systems (Hubau et al., 2020). Nevertheless, 100% of the copper could be leached from the char using the biolixiviant solution.

5.3. Metals recovery and process residues

5.3.1. Metal recovery

The leachate from the char leaching step is a complex mixture of metals. Therefore, the highly selective Acorga reagent was chosen for solvent extraction (SX). A two-stage mixer-settler configuration was proposed followed by electrowinning (EW) which could produce copper cathodes. Direct electrowinning was considered, but discounted given the high iron content of the leachate. Iron management was possible via the precipitation of jarosite and autoclave conversion to hematite.

Within the scope of the project, it was only possible to valorise the copper. It was considered that the precious metals in the leached char residue would be sold directly. However, future work will look at valorising this important fraction within the CEReS process.

5.3.2. Process residues

The solid residue (leached mine wastes) was assessed for subsequent AMD generating potential using standard and novel, biokinetic, AMD-prediction tests. A major element of the CEReS concept is the conversion of environmentally-damaging coal mine wastes into re-usable, stabilised material. Therefore, a significant task was devoted to the development and testing of re-use options (e.g. in civil engineering or mine rehabilitation).

The sulfide component of the coal production waste was almost completely removed by the bioleaching process. Accordingly, the maximum potential acidity (MPA) was reduced. While the amount of sulfate produced during net acid generation tests (NAG) suggested the material was non-acid-forming, intriguingly, the pH of the solution became acidic. Furthermore, negative acid neutralising capacities (ANC) were observed (Bransgrove et al., 2018). Taken together this suggested that the material may be producing acid, but not through the oxidation of residual sulfides. It may be that the 'missing' acid observed in the bioleaching tests is adsorbed to the material and may desorb in the environment. Confirming the long term environmental stability of the leached residues is vital, and so this aspect merits further work.

Four options were considered for the use of the leached coal waste: ceramic products (bricks), production of granulates, and concrete and polymer-concrete products. The addition of leached material (15% initial mass) during brick production had an effect on the final colour, but produced satisfactory bricks with slightly elevated compressive strength. Incorporation into cement products (15%) again had no detrimental effects and slightly improved their compressive strength. Concrete polymer products could be made from the waste alone. However, this required a long bonding time rendering this option impractical.

Finally, the leached waste was tested as a potential substrate for the production of granulates. The granulates produced were of high strength and leachates from them contained permissible levels of potentially toxic substances. Therefore, such granulates can be safely used in underground mining and civil engineering processes and materials and could even be used for combustion (as the waste may contain sufficient residual coal).

6. Process Integration, Economic and Environmental Assessment

Process integration includes efficient use of raw materials, energy efficiency and emissions reduction (Friedler, 2010; Smith, 2000). The implementation of unit operation models within a steady-state simulator enables to facilitate both process integration and flow-sheet optimization (Brochot et al., 2002). The simulator is used to analyse, model and optimize the possible interactions between the equipment in the flow-sheet, in order to maximize resource valorisation, and minimize utilities consumption, operating costs and environmental impact.

6.1.1. Mathematical modelling of unit operations

Modelling of solids material processes relies on two types of model: (i) the unit operation models, designed for determining the different products quality and quantity depending on the feed characteristics and on the equipment parameters (sizes and settings) and (ii) the material models that vary depending on the modelling objectives (such as production performance optimisation, emission or effluent follow-up or energy consumption reduction).

Regarding the PCB catalytic cracking, experimental work had already been carried out on PCBs (Moltó et al., 2009), providing kinetic studies on waste thermal decomposition and identification of the solids residues and of the gaseous emissions. Catalytic pyrolysis models have been developed and applied to different product cracking (Miskolczi et al., 2004; Quek and Balasubramanian, 2012; Yang et al., 2007). The different approaches represent interesting modelling options to be studied for the specific case of PCBs. Those results were be used for defining a first level of material models that have to be enriched through the project experimental work.

Advanced mathematical models for mine tailings bioleaching have been proposed in the literature, enabling the prediction of bioleaching kinetics and particle size reduction (Brochot et al., 2004; d'Hugues et al., 2008; Dreisinger and Abed, 2002) and even to take into account possible concurrent precipitation (Botane et al., 2013).

Several mathematical models for downstream hydrometallurgical operations such as solvent extraction, ion exchange processes or electrowinning are described in literature (Bandyopadhyay et al., 1996; Coetzee, 2003; Coetzee and Petersen, 2005; Gálvez et al., 2005; Saleh et al., 1995). These modelling approaches and methodologies constitute a basis to the development of simplified steady-state models adapted to the processes under development; some of them are already embedded in the simulation platform (USIM PAC) used throughout the project.

CEReS project - GLOBAL SIMULATOR

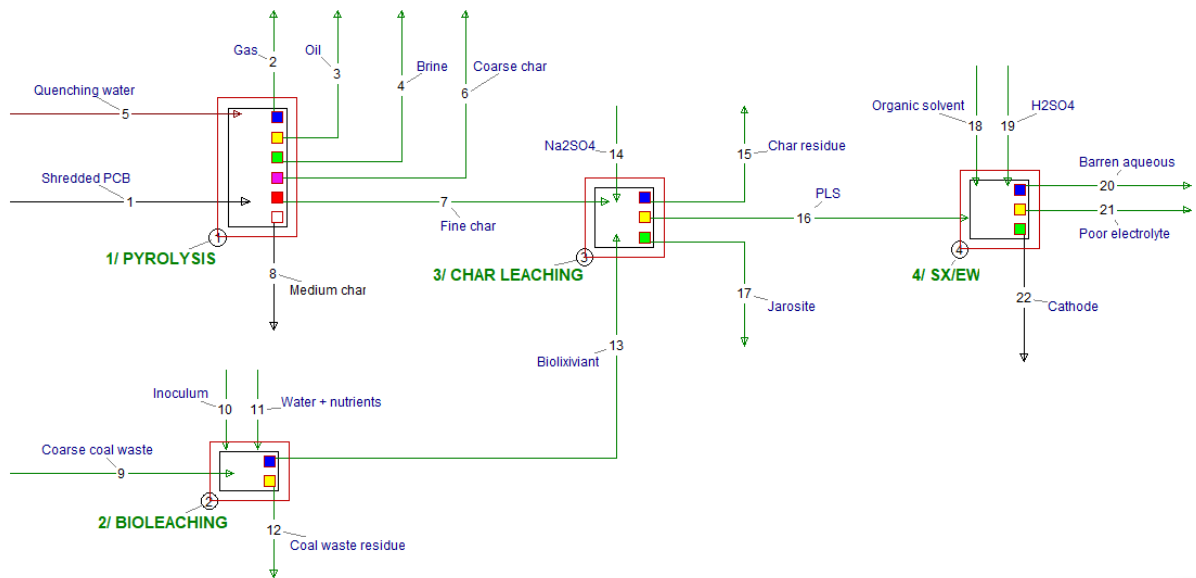


Figure 5. The global CEReS simulator

A global simulator created using USIM PAC, based on the overall process flowsheet, allowed an economic assessment and evaluation of alternative flowsheet options (Figure 5). Based on the pyrolysis of 14,000 t/y of PCB, CEReS would require (and reprocess) 79,000 t/y Janina coal waste producing 76,000 t/y stabilised waste for secondary use, 2,100 t/y enriched char for direct sale to existing processing operations, 923 t/y copper cathode and a final residue containing the precious metals (Figure 6).

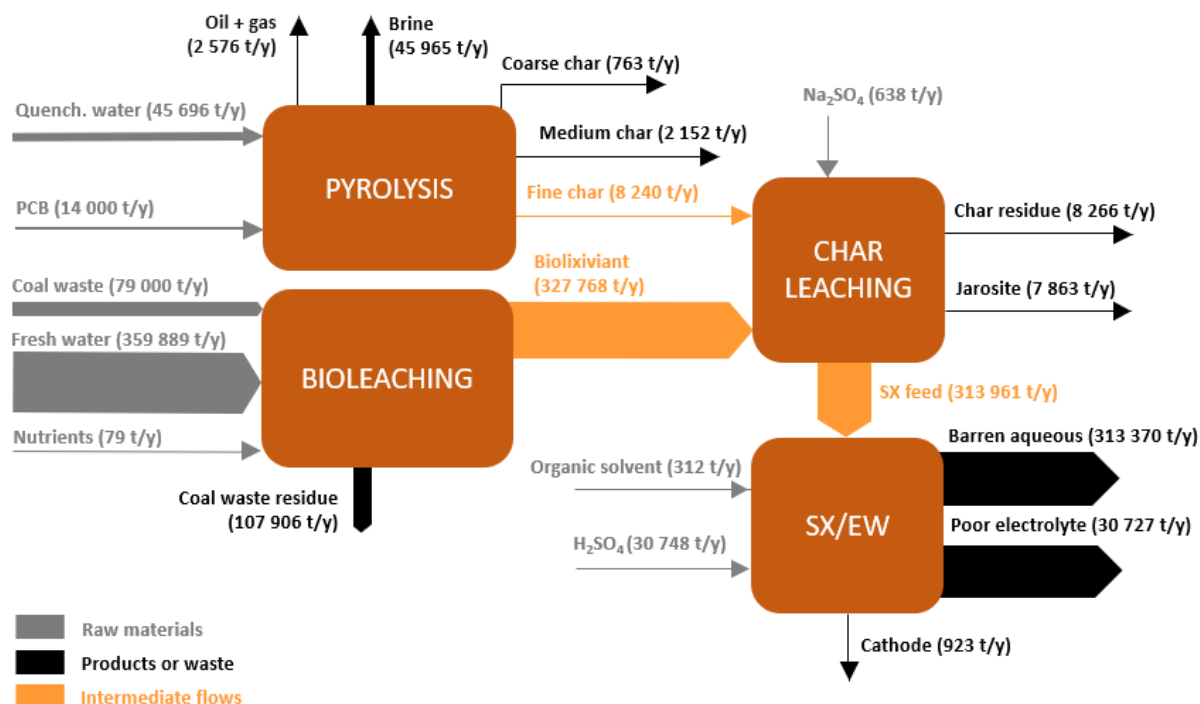


Figure 6. CEReS industrial-scale scenario: global mass balance diagram (original scenario).

The total power demand was estimated to be around 3.9 MW. The main energy-intensive step is the heating of the pregnant leaching solution to 90°C for iron precipitation. Therefore, this option was replaced with simple precipitation using lime, as the additional energy cost could not be justified by the added value from hematite production. This would reduce the energy demand by 46% to 2.1 MW. The second largest energy expenditure item is the first bioleaching tank, mainly due to thermal regulation (cooling system) required as pyrite oxidation is exothermic. In comparison to these uses of energy, that required for coal waste ball milling is significantly lower than the energy required for downstream (bio)-hydrometallurgical operations. Using the software to simulate the incorporation of water recycling loops (of the raffinate to the bioleaching unit, and within the SX/EW circuit) reduced fresh water demand by 88% from around 406 000 to 91 000 m³ *pa* (Figure 7) and results in improved copper recovery.

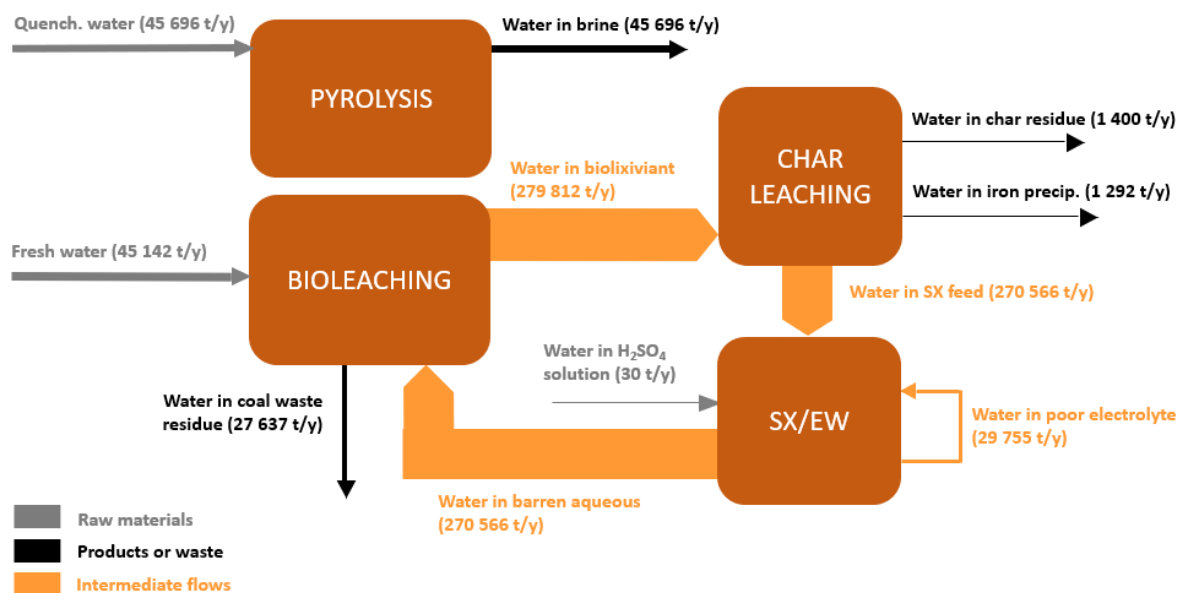


Figure 7. CEReS industrial-scale scenario: water mass balance diagram (refined scenario)

According to the results of Scenario 2, 79 000 tons per year of coal waste can be stabilized through bioleaching, which appears as a solution to the issue of acid mine drainage. 1 334 tons of pure copper are potentially produced by char leaching from 14 000 tons of shredded PCBs. Precious metals may be recovered from char leaching residue to improve the economic balance of the process, but this has not been tested here.

Based on a PCB market value of 1,600€/t, the reprocessing of coal mine waste using CEReS would cost approximately 93 €/t. Such a value is in line with European costs for landfill disposal of this type of waste, but is much higher than the current costs in Poland. However, the current simulation assumes that the stabilised wastes have no value, which may not be the case if, for example, the ceramic or concrete products could be sold. Furthermore, the majority of the PCB value is in the precious metals and the current flowsheet does not include a model for their valorisation. This will be further developed in the future. Overall, there is a need to improve process efficiency and to secure an income from mine waste reprocessing.

6.1.2. Life cycle analysis (LCA)

One of the main objectives of WEEE directive (2012/19/EU)³ is to preserve, protect and improve the quality of the environment, to protect human health and to use natural resources efficiently and rationally. Environmental assessment of the process developed in CEReS will ensure its ability to

³ Directive 2012/19/EU (2012) - Directive on waste electrical and electronic equipment (WEEE)

improve the quality of the environment all along the process life cycle. To achieve this, several methodological gaps were identified and investigated during the project. Waste management and metals recovery environmental assessments are generally studied separately: on the one hand from a waste management perspective and on the other from a metals recovery perspective. In each case, a multi-functionality problem has to be solved. ISO standard (ISO 14044)⁴ and ILCD Handbook⁵ address different ways to solve it: subdivision of process in a multiple of simple process, system expansion and substitution and allocation (physical or economic).

There is abundant literature on life cycle assessment of WEEE recycling but Bigum et al. (2012) note that there are few available life cycle inventories (LCI) data on precious metals. Few data and literature are publicly available on mining industry environmental assessment and mining is generally assessed as a “black box” (Awuah-Offei and Adekpedjou, 2011). Data acquisition at different process development stages within CEReS fulfilled life cycle inventories.

Moreover, mine waste management options are generally neglected in Life Cycle Inventory (LCI) of metal production and particularly of ore production (Reid et al., 2009). The physical phenomena of AMD generation and management options are well documented⁶, but from a life cycle point of view some difficulties arise in the accounting of the longevity of this process (weathering of mine wastes continues for hundreds of years). In LCI, emissions are generally aggregated in time and space and considered as a hot-spot (Heijungs, 1995; Levasseur et al., 2010). Efforts focused on methodological developments in order to take into account time and space specificities in environmental assessments.

A comprehensive LCA of the proposed flowsheet revealed that CEReS was more environmentally friendly than the current “do nothing” scenario in almost all categories (Kouloumpis and Yan, 2019). The process can be highly beneficial for the reduction of toxicity, eutrophication and metal depletion impacts. This is in sync with the initial scope which focuses on the recovery of copper and which is also achieved by minimising the waste stream as well as neutralising the hazardous attributes and valorising more outputs as by-products. The exception was categories linked to fossil fuel use. This is due to the fact the CEReS is a relatively energy-intensive process and Poland’s (the case study country) energy mix is carbon-heavy. If the energy mix in Poland becomes less fossil and carbon intensive in the future or the CEReS method is applied in other EU countries with energy mix of much

⁴ ISO 14044 (2006) – Environmental management – Life cycle assessment – Requirements and guidelines.

⁵ ILCD Handbook (2010) – General guide for life cycle assessment – Detailed guidance. (<http://lct.jrc.ec.europa.eu/assessment/projects>)

⁶ <http://www.brgm.fr/DMA>; www.gardguide.com

lower fossil and carbon intensity (e.g. France), it is possible that the CEReS method can be beneficial for all of the impact categories. Nevertheless, the environmental benefits of CEReS are clear.

7. Conclusions

The project successfully demonstrated the key aspects of the CEReS flowsheet at laboratory and pilot scale. The process was able to convert scrap PCBs into combustible fuels, a halogen brine and a metal-rich char. AMD-generating coal production waste could be stabilised through accelerated weathering and used in construction products. The lixiviant produced was suitable for leaching the copper from the char and this refined into copper cathodes. *In silico* integration and simulation demonstrated the technical viability of the process. The economic assessment, at present, is unfavourable; the process does not create sufficient value to cover the operating costs. While this may improve with enhances in processing efficiency, and certainly if steps are included to recover precious metals, profitability is not necessarily at the heart of the CEReS model. The CEReS concept is built around environmental responsibility and resource recovery. What this project has shown is that co-processing two waste streams can provide a relatively low-cost waste treatment option resulting in demonstrable environmental benefits. The LCA approach validated the environmental advantages of reprocessing such wastes in this way over the current do nothing scenario. The value recovered from the low-grade waste PCBs off-sets the costs of permanently removing the AMD-generating potential from sulfidic wastes resulting in a durable long-term solution.

The extractive industry, and society at large, is facing increasing pressure to find and develop long term, sustainable solutions to handling mine waste. The CEReS process permanently removes the AMD-generating potential from mine wastes, opening the possibility for their use or at least low risk environmental storage. The value recovered from the low-grade waste PCBs off-sets the sulfidic waste processing costs, while also reducing their own environmental burden. The challenge is to improve processing performance so that the cost per ton is less than the current best available options.

8. Acknowledgements

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9. References

Arinanda, M., van Haute, Q., Lambert, F. and Gaydardzhiev, S., 2019. Effects of operational parameters on the bio-assisted leaching of metals from pyrolyzed printed circuit boards. *Miner. Eng.*, 134: 16-22.

- Awuah-Offei, K. and Adekpedjou, A., 2011. Application of life cycle assessment in the mining industry. *The International Journal of Life Cycle Assessment*, 16(1): 82-89.
- Balde, C.P., Wang, F., Kuehr, R. and Huisman, J., 2015. The global e-waste monitor 2014: Quantities, flows and resources.
- Bandyopadhyay, M., Datta, S. and Sanyal, S.K., 1996. A mass transfer model for the hydrometallurgical extraction of Te(IV) by tri-n-butyl phosphate. *Hydrometallurgy*, 43(1): 175-185.
- Bigum, M., Brogaard, L. and Christensen, T.H., 2012. Metal recovery from high-grade WEEE: A life cycle assessment. *J. Hazard. Mater.*, 207–208: 8-14.
- Botane, P., Brochot, S., D'Hugues, P. and Spolaore, P., 2013. Material size distribution in concurrent bio-leaching and precipitation: Experimental procedure and modelling. *Hydrometallurgy*, 133: 7-14.
- Brandl, H., Bosshard, R. and Wegmann, M., 2001. Computer-munching microbes: Metal leaching from electronic scrap by bacteria and fungi. *Hydrometallurgy*, 59(2-3): 319-326.
- Brandl, H., Lehmann, S., Faramarzi, M.A. and Martinelli, D., 2008. Biomobilization of silver, gold, and platinum from solid waste materials by HCN-forming microorganisms. *Hydrometallurgy*, 94(1–4): 14-17.
- Bransgrove, R., Rollinson, G.R., Williamson, B.J. and Bryan, C.G., 2018. Analysis of Sulfidic Coal Production Wastes using Biokinetic Tests Combined with QEMSCAN. In: B. Wills (Ed.), *Sustainable Minerals '18*, Windhoek, Namibia.
- Breivik, K., Armitage, J.M., Wania, F. and Jones, K.C., 2014. Tracking the Global Generation and Exports of e-Waste. Do Existing Estimates Add up? *Environmental Science & Technology*, 48(15): 8735-8743.
- Brochot, S., Durance, M.V., Villeneuve, J., d'Hugues, P. and Mugabi, M., 2004. Modelling of the bioleaching of sulphide ores: application for the simulation of the bioleaching/gravity section of the Kasese Cobalt Company Ltd process plant. *Miner. Eng.*, 17(2): 253-260.
- Brochot, S., Villeneuve, J., Guillaneau, J., Durance, M. and Bourgeois, F., 2002. USIM PAC 3: Design and optimization of mineral processing plants from crushing to refining. Mular, AL, Halbe, DN and Barratt, DJ *Mineral Processing Plant Design, Practice and Control*: 477-494.
- Bryan, C.G. et al., 2015. The use of pyrite as a source of lixiviant in the bioleaching of electronic waste. *Hydrometallurgy*, 152: 33-43.
- Cara, J. et al., 2005. Biodesulphurisation of high sulphur coal by heap leaching. *Fuel*, 84(14): 1905-1910.
- Cardona, I.C. and Márquez, M.A., 2009. Biodesulfurization of two Colombian coals with native microorganisms. *Fuel Process. Technol.*, 90(9): 1099-1106.
- Charbonnier, P., 2001. Management of mining, quarrying and ore-processing waste in the European Union. BRGM service EPI, France.
- Chi, T.D., Lee, J.-c., Pandey, B.D., Yoo, K. and Jeong, J., 2011. Bioleaching of gold and copper from waste mobile phone PCBs by using a cyanogenic bacterium. *Miner. Eng.*, 24(11): 1219-1222.
- Choi, M.-S., Cho, K.-S., Kim, D.-S. and Kim, D.-J., 2004. Microbial Recovery of Copper from Printed Circuit Boards of Waste Computer by *Acidithiobacillus ferrooxidans*. *Journal of Environmental Science and Health, Part A*, 39(11-12): 2973-2982.
- Coetzee, J.W., 2003. An activity model for multi-component ion exchange. *Miner. Eng.*, 16(6): 519-522.
- Coetzee, J.W. and Petersen, F.W., 2005. A simplified resistance model for reversible multicomponent ion exchange. *Hydrometallurgy*, 76(1–2): 19-24.
- Cui, J. and Forssberg, E., 2003. Mechanical recycling of waste electric and electronic equipment: a review. *J. Hazard. Mater.*, 99(3): 243-263.
- Cui, J. and Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: A review. *J. Hazard. Mater.*, 158(2–3): 228-256.

- d'Hugues, P. et al., 2008. Continuous bioleaching of a pyrite concentrate in stirred reactors: Population dynamics and exopolysaccharide production vs. bioleaching performance. *Hydrometallurgy*, 94(1-4): 34-41.
- Dreisinger, D. and Abed, N., 2002. A fundamental study of the reductive leaching of chalcopyrite using metallic iron part I: kinetic analysis. *Hydrometallurgy*, 66(1-3): 37-57.
- EC, 2009. Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities, European Commission.
- EPA, 2011. National Strategy for Electronics Stewardship. In: E.P. Agency (Ed.).
- Eurostat, 2020. Supply, transformation and consumption of solid fossil fuels. In: Eurostat (Ed.).
- Faramarzi, M.A., Stagars, M., Pensini, E., Krebs, W. and Brandl, H., 2004. Metal solubilization from metal-containing solid materials by cyanogenic *Chromobacterium violaceum*. *J. Biotechnol.*, 113(1-3): 321-326.
- Fonti, V., Joulain, C. and Bryan, C.G., 2019. Bioprospecting and the Microbial Ecology of a Coal Production Waste Dump, International Biohydrometallurgy Symposium, Fukuoka, Japan.
- Friedler, F., 2010. Process integration, modelling and optimisation for energy saving and pollution reduction. *Appl. Therm. Eng.*, 30(16): 2270-2280.
- Frosch, R.A., 1992. Industrial ecology: a philosophical introduction. *Proceedings of the National Academy of Sciences*, 89(3): 800-803.
- Gálvez, E.D., Swaney, R.E., Malatesta, C.M. and Cisternas, L.A., 2005. An ASCEND library for the modeling, simulation and optimization of solvent extraction for metal recovery. In: P. Luis and E. Antonio (Eds.), *Computer Aided Chemical Engineering*. Elsevier, pp. 403-408.
- Goodship, V., Stevels, A. and Huisman, J., 2019. Waste electrical and electronic equipment (WEEE) handbook. Woodhead Publishing.
- Gray, N.F., 1997. Environmental impact and remediation of acid mine drainage: a management problem. *Environ. Geol.*, 30(1): 62-71.
- Guezennec, A.-G., Bru, K., Jacob, J. and d'Hugues, P., 2015. Co-processing of sulfidic mining wastes and metal-rich post-consumer wastes by biohydrometallurgy. *Miner. Eng.*, 75: 45-53.
- GUS, 2018. (Główny Urząd Statystyczny - Statistics Poland) Ochrona środowiska 2018, Główny Urząd Statystyczny - Statistics Poland, Warsaw.
- Hallberg, K.B. and Barrie Johnson, D., 2001. Biodiversity of acidophilic prokaryotes, *Adv. Appl. Microbiol.* Academic Press, pp. 37-84.
- He, H. et al., 2012. Biodesulfurization of coal with *Acidithiobacillus caldus* and analysis of the interfacial interaction between cells and pyrite. *Fuel Process. Technol.*, 101: 73-77.
- Heijungs, R., 1995. Harmonization of methods for impact assessment. *Environmental Science and Pollution Research*, 2(4): 217-224.
- Herzig, J., Szczepańska, J., Witczak, S. and Twardowska, I., 1986. Chlorides in the Carboniferous rocks of the Upper Silesian coal basin: Environmental contamination and prognosis. *Fuel*, 65(8): 1134-1141.
- Hoffmann, M.R., Faust, B.C., Panda, F.A., Koo, H.H. and Tsuchiya, H.M., 1981. Kinetics of the Removal of Iron Pyrite from Coal by Microbial Catalysis. *Applied and Environmental Microbiology*, 42(2): 259-271.
- Huang, K., Guo, J. and Xu, Z., 2009. Recycling of waste printed circuit boards: A review of current technologies and treatment status in China. *J. Hazard. Mater.*, 164(2-3): 399-408.
- Hubau, A. et al., 2020. Recovery of metals in a double-stage continuous bioreactor for acidic bioleaching of printed circuit boards (PCBs). *Sep. Purif. Technol.*, 238: 116481.
- Huisman, J. et al., 2008. Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE) Final Report, United Nations University, Bonn, Germany.
- Ilyas, S., Anwar, M.A., Niazi, S.B. and Afzal Ghauri, M., 2007. Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria. *Hydrometallurgy*, 88(1-4): 180-188.
- Jarvis, A. and Younger, P., 2000. Broadening the scope of mine water environmental impact assessment: a UK perspective *Environmental Impact Assessment Review* 20: 85-96.

- Kasper, A.C. et al., 2011. Printed wiring boards for mobile phones: Characterization and recycling of copper. *Waste Manage.* (Oxford), 31(12): 2536-2545.
- Kazadi Mbamba, C., Harrison, S.T.L., Franzidis, J.P. and Broadhurst, J.L., 2012. Mitigating acid rock drainage risks while recovering low-sulfur coal from ultrafine colliery wastes using froth flotation. *Miner. Eng.*, 29: 13-21.
- Khaliq, A., Rhamdhani, M.A., Brooks, G. and Masood, S., 2014. Metal Extraction Processes for Electronic Waste and Existing Industrial Routes: A Review and Australian Perspective. *Resources*, 3(1): 152-179.
- Kingsnorth, D.J., 2011. Meeting the challenges of supply this decade.
- Klein, J., 1998. Technological and economic aspects of coal biodesulfurisation. *Biodegradation*, 9(3): 293-300.
- Kouloumpis, V. and Yan, X., 2019. Life cycle environmental impacts of a novel value-creating method to co-process coal mine and electronic wastes, Society of Environmental Toxicology and Chemistry (SETAC) 2019, Helsinki, Finland.
- Lehner, T., 1998. Integrated recycling of non-ferrous metals at Boliden Ltd. Ronnskar smelter, Electronics and the Environment, 1998. ISEE-1998. Proceedings of the 1998 IEEE International Symposium, pp. 42-47.
- Levasseur, A., Lesage, P., Margni, M., Deschênes, L. and Samson, R., 2010. Considering Time in LCA: Dynamic LCA and Its Application to Global Warming Impact Assessments. *Environmental Science & Technology*, 44(8): 3169-3174.
- Lewis, G., Gaydardzhiev, S., Bastin, D. and Bareel, P.-F., 2011. Bio hydrometallurgical recovery of metals from Fine Shredder Residues. *Miner. Eng.*, 24(11): 1166-1171.
- Liang, G., Mo, Y. and Zhou, Q., 2010. Novel strategies of bioleaching metals from printed circuit boards (PCBs) in mixed cultivation of two acidophiles. *Enzyme Microb. Technol.*, 47(7): 322-326.
- Lottermoser, B., 2010. *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg.
- Lottermoser, B.G., 2011. Recycling, Reuse and Rehabilitation of Mine Wastes. *Elements*, 7(6): 405-410.
- Luda, M.P., 2011. Recycling of Printed Circuit Boards. In: S. Kumar (Ed.), *Integrated Waste Management*. InTech, pp. 285-298.
- Lundstedt, S., 2011. Recycling and disposal of electronic waste: Health hazards and environmental impacts, Swedish Environmental Protection Agency.
- Mark, F.E. and Lehner, T., 2000. Plastics recovery from waste electrical & electronic equipment in non-ferrous metal processes. *Association of plastics manufactures in Europe*: 1-23.
- Milan, A.D., Ahmadi, A. and Hosseini, S.M.R., 2017. Biodesulfurization of a Coarse-Grained High Sulfur Coal in a Full-Scale Packed-Bed Bioreactor. *Solid State Phenomena*, 262: 207-210.
- Miskolczi, N., Bartha, L., Deák, G.Y., Jóver, B. and Kalló, D., 2004. Kinetic Model of the Chemical Recycling of Waste Polyethylene into Fuels. *Process Safety and Environmental Protection*, 82(3): 223-229.
- Moltó, J., Font, R., Gálvez, A. and Conesa, J.A., 2009. Pyrolysis and combustion of electronic wastes. *J. Anal. Appl. Pyrolysis*, 84(1): 68-78.
- Morin, D.H.R. and d'Hugues, P., 2007. Bioleaching of a cobalt-containing pyrite in stirred reactors: a case study from laboratory scale to industrial application, *Biomining*. Springer, pp. 35-55.
- Nnorom, I.C. and Osibanjo, O., 2008. Overview of electronic waste (e-waste) management practices and legislations, and their poor applications in the developing countries. *Resources, Conservation and Recycling*, 52(6): 843-858.
- Oguchi, M., Sakanakura, H., Terazono, A. and Takigami, H., 2012. Fate of metals contained in waste electrical and electronic equipment in a municipal waste treatment process. *Waste Manage.* (Oxford), 32(1): 96-103.

- Olson, G.J. and Kelly, R.M., 1991. Chemical and microbiological problems associated with research on the biodesulfurization of coal. A review. *Resources, Conservation and Recycling*, 5(2): 183-193.
- Ors, N., Rossi, G., Trois, P., Valenti, P.D. and Zecchin, A., 1991. Coal biodesulfurization: design criteria of a pilot plant. *Resources, Conservation and Recycling*, 5(2): 211-230.
- Östensson, O., 2006. Mineral and metals production: an overview. Caromb Consulting, Stockholm.
- Papadimitriou, E.K., Barton, J.R. and Stentiford, E.I., 2008. Sources and levels of potentially toxic elements in the biodegradable fraction of autoclaved non-segregated household waste and its compost/ digestate. *Waste Manage. Res.*, 26(5): 419-430.
- PHA, 2006. ELECTRONIC WASTE RECOVERY STUDY, PHA Consulting Associates, Nova Scotia.
- Quek, A. and Balasubramanian, R., 2012. Mathematical modeling of rubber tire pyrolysis. *J. Anal. Appl. Pyrolysis*, 95: 1-13.
- Rawlings, D.E. and Johnson, D.B., 2007. *Biomining*. Springer Berlin Heidelberg.
- Reid, C., Bécaert, V., Aubertin, M., Rosenbaum, R.K. and Deschênes, L., 2009. Life cycle assessment of mine tailings management in Canada. *Journal of Cleaner Production*, 17(4): 471-479.
- Rivero-Hudec, M.A., Sodhi, M. and Goglia-Arora, D., 2009. Biorecovery of Metals from Electronic Waste, 7th Latin American and Caribbean Conference for Engineering and Technology, San Cristóbal, Venezuela.
- Rossi, G., 2014. The Microbial Desulfurization of Coal. In: A. Schippers, F. Glombitza and W. Sand (Eds.), *Geobiotechnology II: Energy Resources, Subsurface Technologies, Organic Pollutants and Mining Legal Principles*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 147-167.
- Saleh, M.M., Weidner, J.W. and Ateya, B.G., 1995. Electrowinning of Non-Noble Metals with Simultaneous Hydrogen Evolution at Flow-Through Porous Electrodes: I . Theoretical. *J. Electrochem. Soc.*, 142(12): 4113-4121.
- Schippers, A., Rohwerder, T. and Sand, W., 1999. Intermediary sulfur compounds in pyrite oxidation: implications for bioleaching and biodepyritization of coal. *Appl. Microbiol. Biotechnol.*, 52(1): 104-110.
- Smith, R., 2000. State of the art in process integration. *Appl. Therm. Eng.*, 20(15–16): 1337-1345.
- Stefaniak, S. and Twardowska, I., 2010. Impact of engineering constructions made of carboniferous waste rock on groundwater deterioration. In: C. Wolkersdorfer and A. Freund (Eds.), *International Mine Water Association Symposium – Mine Water and Innovative Thinking*, Sydney, NS, pp. 599-602.
- Szczepańska-Plewa, J., Stefaniak, S. and Twardowska, I., 2010. Coal mining waste management and its impact on the groundwater chemical status exemplified in the Upper Silesia coal basin (Poland). *Biuletyn Państwowego Instytutu Geologicznego, Hydrogeologia*, 441: 157-166.
- Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y. and Deveci, H., 2012. Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling. *Miner. Eng.*, 25(1): 28-37.
- Verburg, R., Bezuidenhout, N., Chatwin, T. and Ferguson, K., 2009. The global acid rock drainage guide (GARD Guide). *Mine Water Environ.*, 28(4): 305.
- Vestola, E.A. et al., 2010. Acid bioleaching of solid waste materials from copper, steel and recycling industries. *Hydrometallurgy*, 103(1–4): 74-79.
- Wang, J., Bai, J., Xu, J. and Liang, B., 2009. Bioleaching of metals from printed wire boards by *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and their mixture. *J. Hazard. Mater.*, 172(2–3): 1100-1105.
- Widmer, R., Oswald-Krapf, H., Sinha-Khetriwal, D., Schnellmann, M. and Böni, H., 2005. Global perspectives on e-waste. *Environmental Impact Assessment Review*, 25(5 SPEC. ISS.): 436-458.
- Xiang, Y. et al., 2010. Bioleaching of copper from waste printed circuit boards by bacterial consortium enriched from acid mine drainage. *J. Hazard. Mater.*, 184(1–3): 812-818.
- Yang, T., Xu, Z., Wen, J. and Yang, L., 2009. Factors influencing bioleaching copper from waste printed circuit boards by *Acidithiobacillus ferrooxidans*. *Hydrometallurgy*, 97(1–2): 29-32.

- 919 Yang, Y.B., Phan, A.N., Ryu, C., Sharifi, V. and Swithenbank, J., 2007. Mathematical modelling of slow
920 pyrolysis of segregated solid wastes in a packed-bed pyrolyser. *Fuel*, 86(1–2): 169-180.
921 Zhu, N. et al., 2011. Bioleaching of metal concentrates of waste printed circuit boards by mixed
922 culture of acidophilic bacteria. *J. Hazard. Mater.*, 192(2): 614-619.
923