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A Review on The Sustainable Production of Copper Nanoparticles from Waste Copper Dust using Nanometer-Scale Zerovalent Iron Particles as Reducing Agent

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Abstract

This Century will see an urgent up-scaling in the global production of copper nanoparticles due to the continuous industrial development and mounting need to address pressing global issues including non-pharmaceutical disease management and climate change. Mining, benefaction, refining, reagent synthesis, and finally nanoproduct synthesis are the typical linear multistage steps in the traditional copper nanoparticle synthesis process, which is energy and resource intensive. The utilization of nanometer-scale zerovalent iron particles as a reducing agent for environmentally friendly copper nanoparticle manufacturing from waste copper dust is discussed in this paper. Based on the revision, it is clear that this method has significant potential and could represent a completely new paradigm for the conversion of low-grade Cu bearing waste (such as waste copper dust) into useful nanoparticulate Cu compounds for a variety of industrial applications.

Keywords: waste copper dust; cementation; chemical reduction; hydrometallurgy; valorization

Abbreviations

WCD: waste copper dust.
Cu-NPs: copper, copper (I), and copper (II) oxide nanoparticles.
nZIP: nanometer-scale zerovalent iron particles.

Introduction

As shown in Table 1, copper (Cu) is the element with the highest percentage content in the majority of waste copper dust (WCD). If this WCD are disposed of improperly, hazardous substances would cause severe environmental issues and a great deal of valuable Cu would be lost. Consequently, unusual considerations for waste treatment and the recovery of Cu values have increased as a result of WCD recycling [1]. Many different technologies have been proposed recently to recover Cu from WCD [2-12].

Chemical Composition of WCD (%)										***Reference***
Cu	***Fe***	***Zn***	***S***	***Bi***	***As***	***Cd***	***Pb***	***Sb***	***others***	
18.02	13.36	0.27	3.44	0.002	-	-	0.12	-		Okanigbe, Popoola, Adeleke [5]
10.9	1.6	7.8	-	1.9	7.1	1.3	14.2	0.1	55.1	Ha et al. [13]
7.53	-	40.21	-	-	-	-	6.62	-	45.64	Qiang et al. [14]
41.7	29.6	0.3	13.0	2.3	0.4	0.0	0.3	-	12.4	Vítková et al. [15]
35.5	15.3	-	12.2	-	-	-	-	-	55.5	Bakhtiari et al.[16]
33.7	21.2	-	9.0	-	0.8	-	6.6	-	28.7	Vakylabad et al. [17, 18]
27.0	11.0	5.8	7.5	0.2	13.0	0.2	1.50	-	33.8	Morales et al. [19]
10.8	0.8	15.6	10.4	3.5	19.4	-	7.80	0.1	31.6	Montenegro et al. [20]
24.5	14.0	0.2	-	-	0.9	-	0.1	-	60.4	Alguacil et al.[21]
4.0	-	18.0	7.0	1.1	20.5	9.5	8.0	1.2	-	Font et al. [22]

Table 1: Chemical Compositions of different WCD from around the world [6].

However, significant interest has been focused on recovering Cu from WCD as copper nanoparticles (Cu-NPs) by numerous researchers [6, 23, and 24]. This is as a result of its fascinating attributes and prospective applications in numerous fields.Cu-NPs' astounding catalytic, optical, and electrical conducting characteristics have caused a great deal of concern [25, 26].

Recently, several researchers have proposed various techniques for producing Cu-NPs from WCD, including thermal decomposition of copper precursor from low grade WCD [6, 23, 24, 27, and 28]. It was challenging to control the size of the prepared Cu-NPs in the majority of these methods.

Due to the complicated composition of these WCD (Table 1), it is obvious that the notion of obtaining Cu-NPs from them is undoubtedly a difficult undertaking. In order to produce Cu-NPs from WCD sustainably, it is necessary to revise existing synthesis pathways as well as a nonconventional synthesis route that can reinvent mining technology, which is the motivation behind this appraisal.

Background

Metallic nanoparticles are essential for providing technology solutions to 21st-century global concerns. There is a strong argument in favor of the development of environmentally friendly methods for the mass production of these materials in order to facilitate important applications in chemical synthesis, carbon cycle closure, increasing agricultural productivity, and non-pharmaceutical antimicrobials for combating the concurrent threat of global pandemics and the rising prevalence of drug-resistant pathogens. The following is a quick explanation of some relevant examples for copper, copper (I), and copper (II) oxide nanoparticles (hence referred to as Cu-NPs):

Applications of Cu-NPs

The broader spectrum of uses for nanoscale Cu/CuOx catalysts is described by Gawande et al. [29] and includes reduction, oxidation, A3-coupling, electrocatalysis, photocatalysis, and gas-phase processes. One of the cornerstones of a global strategy for closing the carbon loop to fight climate change is the use of CO_2 as a chemical feedstock. An appealing method to do this is the electrochemical reduction of CO_2 to useful chemicals including formic acid, methanol, syngas, and higher hydrocarbons [30]. Metallic catalysts are used in the process, and nanostructured Cu/CuO is known to be particularly promising owing to its high Faradic efficiencies and low over potentials [31]. Cu has long been known to be an effective antibacterial, showing bactericidal, fungicidal, and viricidal activity when used as Cu-NPs [32].

Effectiveness against dangerous bacteria like Staphylococcus aureus, fungus like Candida albicans, and the influenza virus are some specific examples [33]. Cu-NPs could be used or incorporated into food packaging, personal protective equipment, water disinfection, membrane applications for controlling biofouling, and antimicrobial composites, coatings, and textiles [34].

By 2050, it is anticipated that there will be close to 10 billion people on the planet, which would result in a corresponding rise in food demand [35, 36]. Cu-NPs may be an important component of sustainable agriculture in this situation. Cu-NPs have been used in agritech applications as fertilizers or fungicides [37, 38], or they may be effective by indirectly influencing the soil microbiome, which could increase the efficiency of nutrient consumption and nitrogen fixation [39].

Cu-NPs, for instance, have been demonstrated to promote soybean development in the field of agriculture [40] and may even play a part in the biofortification of crops, especially those cultivated on alkaline soils [41]. Cu-NPs have a wide range of additional potential uses, such as improving emissions from the combustion of fuels, such as biodiesel [42], in conductive inks [43], as additives in lubricants and polymers [44, 45], and as a cooling water additive to increase heat conductivity [46].

Conventional synthesis routes for Cu recovery from WCD

When recovering and recycling resources from WCD, one or more extractive metallurgy unit activities are usually combined. A number of reports on the management of WCD have been published in the literature, and they were briefly encapsulated as process flow diagrams (PFD).

According to Li et al. [47] PFD's (i.e. Figure 1), arsenic is removed from the WCD leach solution via co-precipitation with ferric ions.

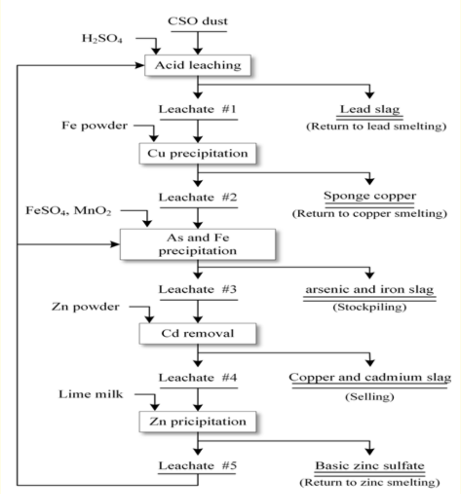

Figure 1: Arsenic is removal from WCD leach solution via co-precipitation with ferric ions [47].

The recovery of precious metals and the removal of arsenic from WCD have both been extensively investigated using the pyro-hydrometallurgical method [48]. Figure 2 serves as a PFD and shows the technique as described by the author.

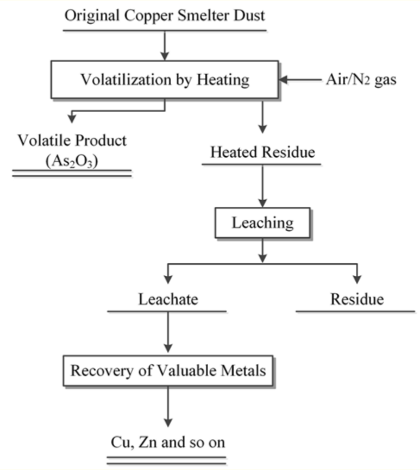

Figure 2: the pyro-hydrometallurgical PFD for treatment of WCD [48].

The bioleaching of WCD from smelters in Iran's Sarcheshmeh copper complex was studied by Bakhtiari et al. [49]. Recirculating the dust to the smelters was the researchers' initial strategy, but they soon recognized that this approach decreased furnace efficiency while raising the energy needed for smelting. Bakhtiari et al. [49] assert that the dust bio-treatment process consumes acid despite the fact that oxidation of sulphide minerals (especially pyrite) in copper concentrates results in the release of acid. The complete procedure is shown as a PFD for clarity's sake (Figure 3).

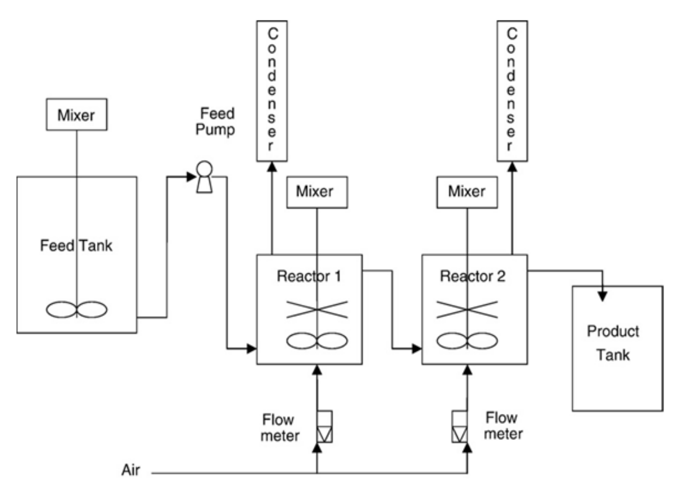

Figure 3: A simple PFD for the continuous copper recovery from a WCD in stirred tank reactors [49].

The bioleaching of copper from the Sarcheshmeh copper smelting plant's WCD was studied by Bakhtiari et al. [16]. In the study, the outcomes of a series of continuous tests performed on two-stage airlift bioreactors injected with bacteria that were originally produced from acid mine drainage were described. Figure 4 summarizes the sequential procedures needed to recover the metal value.

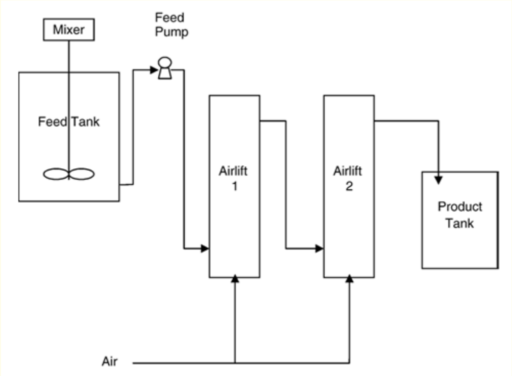

Figure 4: A straightforward PFD for copper bioleaching from WCD in a succession of airlift bioreactors [16].

Gao et al. [4] claim that WCD is an ultrafine hazardous waste that contains numerous heavy metallic elements. Through unit operations of zinc vapor evaporation and condensation as well as super-gravity separation of copper droplets, they suggested a novel method to effectively recover crown zinc and metallic copper from WCD. They referred to this method as a PFD (Figure 5).

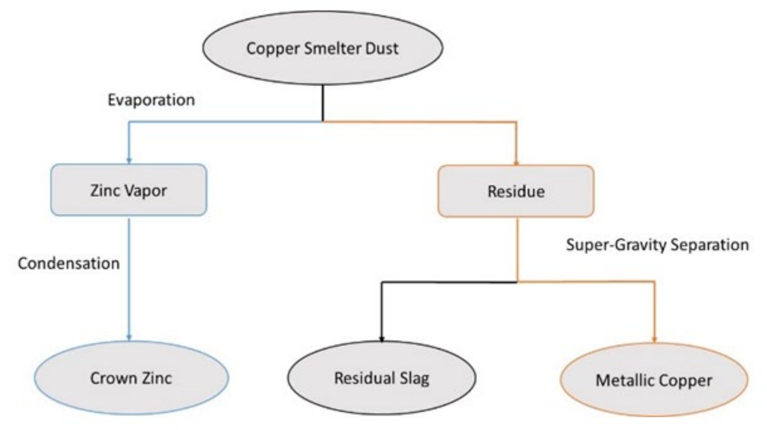

Figure 5: Evaporation, condensation, and super-gravity separation are used to recover crown zinc and metallic copper from WCD [4].

According to Ha et al. [13], secondary products, including WCD, are abundant in bismuth (Bi) and other significant metals. In their research, they described a productive hydrometallurgical technique for extracting Bi from WCD. H_2SO_4 and NaCl can be used as leaching reagents to remove Bi from WCD with a 92% leaching efficiency under ideal circumstances. Figure 6 provides a summary of the unit activities in this PFD.

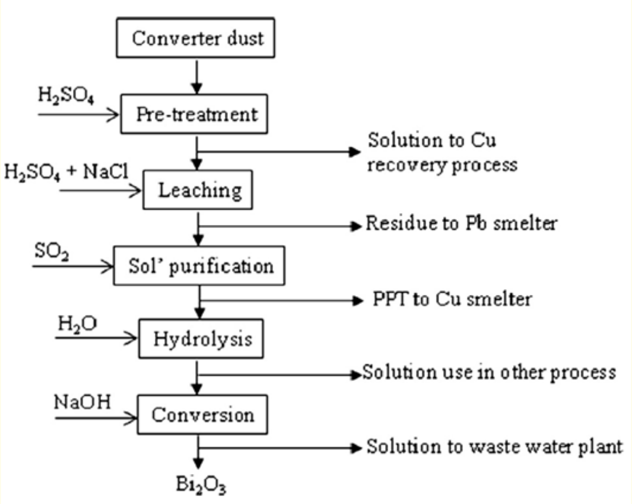

Figure 6: Process Flow Diagram for Bi Recovery from WCD [13].

Soon after copper and zinc were recovered from WCD in the work of Chen et al. [50], resource recovery and recycling from WCD for Bi was attained. Figure 7 shows the PFD for the unit techniques used in the recovery.

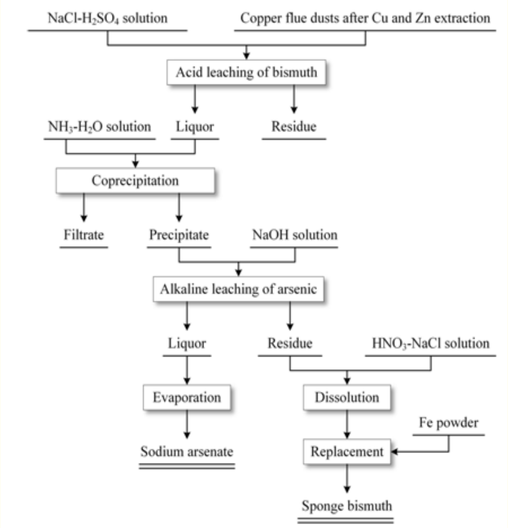

Figure 7: PFD for Bi recovery from WCD [50].

By employing NaOH-Na_2S to leach the WCD, Guo et al. [51] established a hydrometallurgical process to achieve the selective recovery of arsenic from WCD. For ease of comprehension and reproducibility, the complete process was well represented as a PFD (Figure 8).

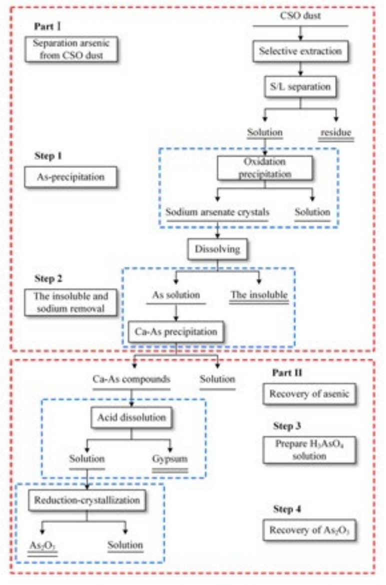

Figure 8: PFD for arsenic recovery from WCD [51].

In order to treat WCD using oxidative acid leaching, Zhang et al. [52] substituted waste acid for sulphuric acid as the leaching media. This method is illustrated as a PFD in Figure 9.

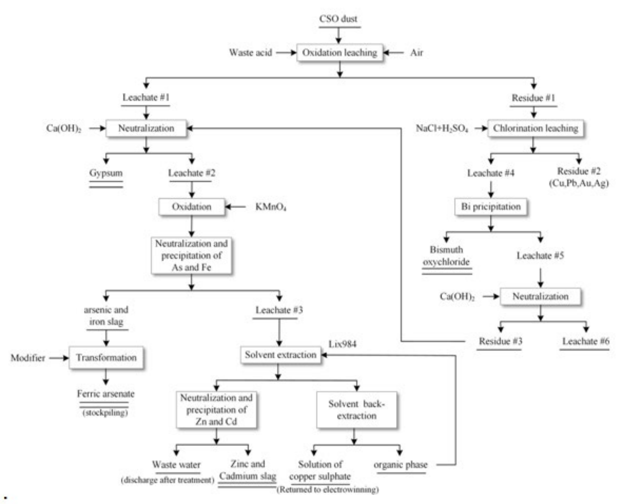

Figure 9: PFD for treatment of WCD [52].

N_9O_2 and P_2O_4 extractants were used by Jia et al. [53] to extract and separate copper and zinc from solution. Then, a PFD was used to express this technique (Figure 10).

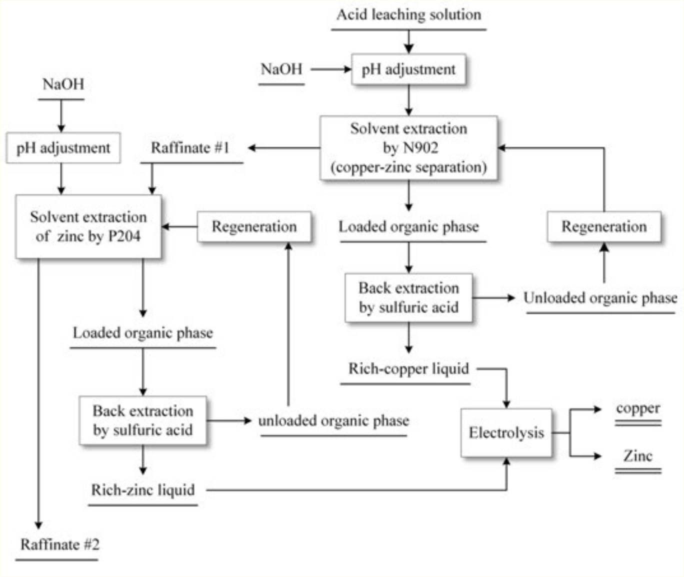

Figure 10: PFD for extraction and separation for Cu and Zn from WCD [53].

According to Shibayama et al. [54], smelting waste products such smelter slag, flue gas, valuable metals, and hazardous chemicals are inextricably generated as secondary products during the pyrometallurgical processing of non-ferrous metals. For these materials to reduce environmental loading and recover important metals, suitable treatment methods are required. On the other hand, their alternate pyrometallurgy-hydrometallurgy method was outlined as a PFD (Figure 11).

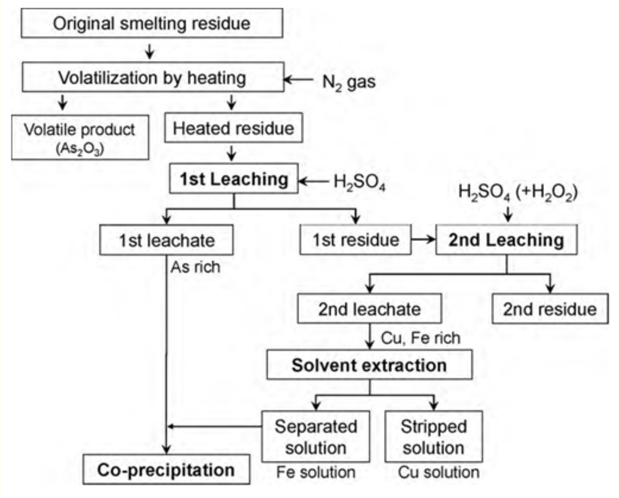

Figure 11: Arsenic removal from WCD and high purity copper recovery PFD [54].

According to Pérez-Moreno et al. [55], WCD is created during the cleaning of copper slag, and its reprocessing results in the production of harmful contaminants. Due to the high metal content, neither the economy nor the environment are benefited by their disposal. Given the foregoing, the main objective was to better understand how these wastes (SWC and CFD) could be reused in different fields, as shown by the PFD in Figure 12.

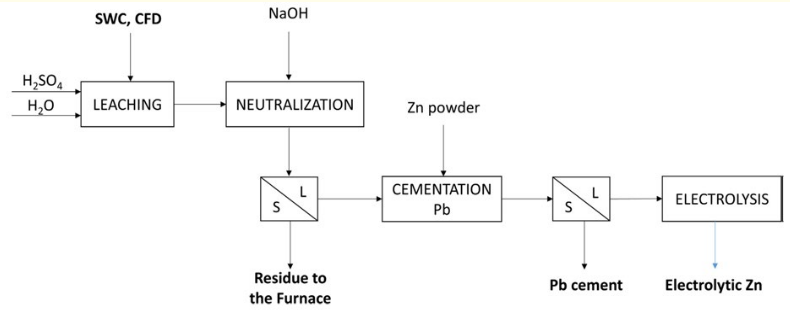

Figure 12: PFD of the proposed SWC and CFD treatment [55].

Conventional Cu-NPs synthesis routes

Cu-NPs recovery from other copper resources

It is obvious that the wide range of large-scale applications described above calls for equivalent methods of environmentally friendly and economically viable Cu-NPs mass production, which will otherwise restrain the adoption of these game-changing technologies. Electrochemical deposition [56], hydrothermal [57, 58], precipitation [59], microwave aided [60], solid state synthesis [61], and mechanochemical synthesis [62] are some of the current batch synthesis techniques. Arc/spark techniques and continuous hydrothermal flow synthesis with supercritical water [63], have both been used to accomplish continuous/larger-scale production, and when paired with confined jet mixer, are reported to produce kg/day quantities [64].

It is obvious that there is currently a significant mismatch between the level of production described in the literature and the extremely huge quantities of Cu-NPs required to satisfy the variety of prospective commercial uses. It is accepted that there are few life cycle assessment studies on the production of nanomaterials from an environmental sustainability perspective [46]. However, there are already significant “in-built” environmental footprints connected with the initial production of the precursor Cu reagents, regardless of the Cu-NPs synthesis method chosen (i.e. starting with mining and beneficiation of Cu from its ore, which is then followed by a series of purification and chemical engineering steps in order to yield the final Cu reagent raw material, usually as water soluble salt).

In 2018, physical excavation mining techniques were used to remove more than 99% of the mass of all metals and metalloids from the Earth, with open cast techniques accounting for the vast majority [65]. By definition, it is an invasive operation that involves completely physically removing topsoil, overburden rock, and any accompanying biological residents in order to access the ore.

The ore then always needs to be beneficiated, which usually involves removing gangue material (typically >90% by volume) at a specially designed plant. Overall, the process produces staggeringly vast amounts of solid trash, currently averaging 20 billion tonnes year, or around 20 times more than the total amount of municipal waste generated worldwide [66, 67]. On a local and regional level, negative effects have included significant and irreversible habitat damage, contaminating ground and surface waters with ecotoxic metals and/or acidic/alkaline pH mine water, and the aeolian migration of ecotoxic dust over extremely large distances [68].

These issues might put mining companies’ ability to conduct business in jeopardy, and poorly run mines could have devastating effects on ecosystems and human health. Mining continues to be one of the major industrial contributors to global CO_2 emissions due to the substantial energy requirements of transporting, crushing, and processing billions of tonnes of material. This makes it obvious that methods to reduce Cu-NPs's lifespan impacts from cradle to grave need to be included in sustainable routes to mass production, and that this mass production needs to be combined with sustainable mining techniques [69].

Cu-NPs recovery from WCD

Figure 2 depicts the traditional approach recommended by Bakhitiari [27], for Cu-NPs from WCD. This method uses harmful chemicals to handle the problem of pollutants and has 8 unit operations. These substances are not environmentally friendly. In contrast, the technology for the study is proposed by Okanigbe [28] and uses 6 unit operations, 2 fewer than the technology employed by Bakhitiari [27]. Additionally, this technique considers the reduction or elimination of impurities using a water-based, economically viable, and environmentally favorable medium.

Due to the intricacy of WCD's chemical makeup, as shown in Table 1, producing Cu-NPs from WCD in a single step is still a difficult operation.

Use of nanometer-scale zerovalent iron particles (nZIP) as a selective reducing agent for sustainable Cu-NPs production

The purpose of this research is to demonstrate the feasibility of using nZIP as a magneto-responsive chemical reducing agent for the selective recovery of copper from its parent ore. The reductive precipitation of Cu from the aqueous phase is made possible by the fact that Cu is higher on the galvanic series than Fe [70], as described in Eq. 1 that follows:

$$Fe^{0}_{(s)} + Cu^{2+}_{(aq)} = Fe^{2+}_{(aq)} + Cu^{0}_{(s)} \quad E^{0}= 0.78\ V\text{……………………(Eq. 1)}$$

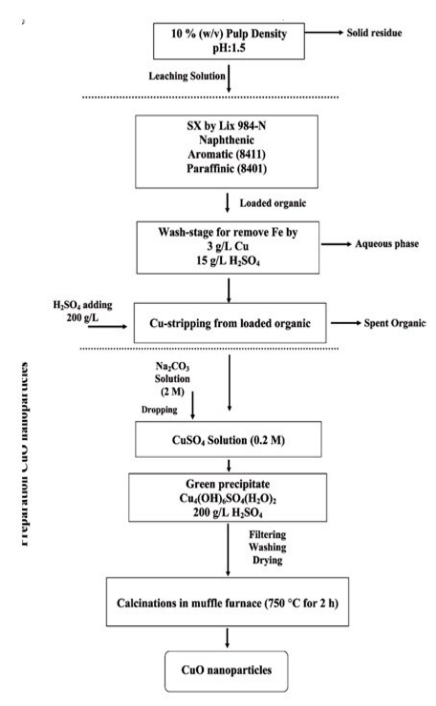

Figure 13: PFD for recovering copper as Cu-NPs from WCD [13].

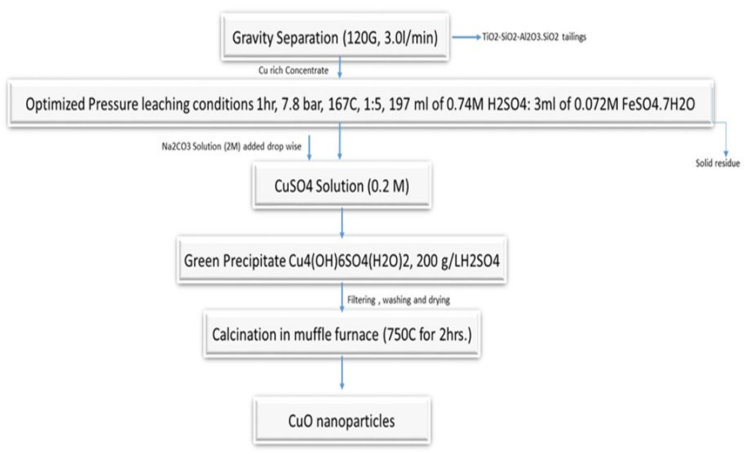

Figure 14: PFD for Cu recovery from South Africa's WCD [28].

For their reduction to a metallic state, several common metals likewise show lower standard electrode potentials (E^0) than Fe^{2+} (-0.44 V), including: K^+ (-2.92 V), Ca^{2+} (-2.84 V), Na^+ (-2.71 V), Mg^{2+} (-2.37 V), Mn^{2+} (-1.18 V) and Zn (-0.76 V), and, when exposed to Fe0, frequently stay in the aqueous phase. Because of this, the reaction between Fe and Cu can be very selective [70]. Although bulk scale Fe0 has been extensively investigated for these purposes [71], nothing is currently known about the comparative effectiveness of nZIP and the physicochemical characteristics of the resulting Cu-bearing (nano) precipitates.

In situ (i.e., subsurface or "in-pulp") injection of nZIP into a target zone (e.g., a leached high grade ore body) followed by in situ nCu synthesis and magnetic recovery is possible thanks to the superior specific surface area of nZIP and its fast reaction kinetics. However, its transformative potential is likely due to its nanometer scale, which when combined with its (super) paramagnetic behavior and ability to act as The end result is the simple, one-step "translocation of Cu-NPs synthesis into the subsurface," which presents an opportunity to move past the conventional paradigm of mining, benefaction, refining, Cu-reagent synthesis, and Cu-NPs product synthesis, which is currently linear and multistep.

Industrial/environmental implications

Use of nZIP as an agent for selective Cu-NPs synthesis

Cu-NPs are created primarily by the cementation of aqueous Cu with nZIP, which involves the heterogeneous reduction of Cu^{2+} to Cu^0 on nZIP and the simultaneous dissolution of Fe from the nZIP to form discrete Cu^0 nanoparticles (Eq. 1). The spontaneous reaction produces a 1:1 molar ratio chemical reduction of Cu^{2+} to Cu^0 together with the oxidation of Fe^0 to Fe^{2+}.

The creation of Cu^0/Cu_2O nanoparticles with a well-constrained particle size distribution from malachite ore has been demonstrated here using a straightforward one-pot approach. It is obvious that applying a suitable reductant for the mass-production of the nZIP is necessary in order to use nZIP as the reductant in the manufacture of the Cu-NPs. However, utilizing nZIP as an intermediate reductant could have a number of significant benefits.

Due to nZIP's extensive application in environmental cleanup, large-scale production has already been created. According to Stefanowicz, Osiska, and Napieralska-Zagozda [71], there are "top down" ways of lithographic grinding and precision milling as well as "bottom up" methods including chemical and carbothermal reduction, electrochemistry, and green synthesis processes. The price difference between bulk copper and iron could provide as a sufficient "circular economy" and economic motivation for the grinding and milling routes.

For instance, as of 9:19 a.m. on October 25, 2022, the price of scrap steel is R6.59/kg ($0.36/kg, £0.32/kg), according to Gauteng scrap metal pricing [72], while recent values for Cu-NPs might range from R833,62-R1042,02/kg ($45,12-$56,4/kg, £40.00 - £50.00/Kg) for well confined Cu-NPs (e.g. Alibaba.com [73]). There are also several potential scenarios whereby nZIP could be made cheaply and sustainably using waste materials/waters. Key examples include acid mine drainage, pickling sludge, WCD, waste iron dust and waste aluminium dust.

Reinventing mining technology for sustainable Cu-NPs production from waste copper dust

A target resource, such as a metal, is selectively extracted from its host material, such as an ore body, waste, or wastewater, in situ, and then transported to the surface for recovery. This technique is known as precision mining [74]. The requirement that resource recovery be accomplished with the least possible impact on the host material or environment and with the least amount of waste is an inherent design characteristic of precision mining.

The use of magnetic nanoparticles as remotely operated sorbents and/or delivery vehicles for resource recovery is one approach that could be extremely useful. Other approaches are also possible. Because malachite is a valuable mineral and commodity on a global scale, we have utilized the recovery of Cu from malachite ore as our example in this article. Due to their capacity to dissolve Cu even when used at very low concentrations, H_2SO_4 and CH_3COOH were shown to be acceptable lixiviants (i.e. 0.5M).

This is a key component of the Precision Mining strategy because it makes it possible to dissolve the target metal with the least amount of chemical disturbance to the host media.

The results also show that a strong or weak base can be used to partially neutralize H_2SO_4 or CH_3COOH before the addition of nZIP. This procedure had the secondary benefit of further reducing the acidity of the Cu-NPs while its primary goal was to establish favorable pH conditions for selective Cu-NPs precipitation.

Due to the Fe-Cu cementation reaction's inherent selectivity, this Cu-NPs precipitation was noted as being very selective. Results also show that an externally applied magnetic field can successfully recover nCu because it is entrained with residual (super) paramagnetic nZIP [75]. According to HRTEM examination, the entrained Cu-NPs precipitate was in the form of discrete nanoparticles, making it likely that they could be easily removed from the nZIP (e.g. via centrifugation or selective dissolution).

The use of nZIP for the production of selective Cu-NPs may also be combined with ex situ ore processing. Cu recovery from low-grade ores and boosting recovery efficiency from Cu leach slurries with poor filterability and/or settling characteristics are two recent applications of “in pulp” technologies (such as resin in pulp, RIP). The main benefit of this is the avoidance of large liquid-solid ratios while performing such hydrometallurgical operations, which reduces the high cost of slurry filtering and treatment of the filtrate [76].

Despite these advantages, RIP is still a little-used technique, largely because of worries about the longevity and reusability of such resins [77]. In contrast, “nZIP in pulp” could achieve the benefits of in-pulp techniques with the extra advantage of directly converting Cu to a useful nanoproduct. If unreacted nZIP is still entangled with the copper product, magnetic separation, the use of deflocculants like $Na_4P_2O_7$, or physical techniques like sonication may also be used to separate the pulp from the product nanoparticles.

Conclusions

There is enormous potential for the sustainable manufacture of Cu-NPs from WCD employing nanometer-scale zerovalent iron particles as the reducing agent, which will be necessary for many of the biggest technical challenges of this century. This could represent a whole new paradigm for the production of useful nanoparticulate Cu compounds for a variety of industries and applications from low-grade Cu ore and Cu-bearing waste (such the WCD).

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References

1. Rao SR Ramachandra. “Resource recovery and recycling from metallurgical wastes”. Elsevier (2011).
2. Yang Tianzu., et al. “Hydrometallurgical treatment of copper smelting dust by oxidation leaching and fractional precipitation technology”. JoM 69.10 (2017): 1982-1986.
3. Xue J., et al. “Comprehensive recovery of arsenic and antimony from arsenic-rich copper smelter dust”. Journal of Hazardous Materials 413 (2021): 125365.
4. Gao Jintao., et al. “Recovery of crown zinc and metallic copper from copper smelter dust by evaporation, condensation and super-gravity separation”. Separation and Purification Technology 231 (2020): 115925.
5. Okanigbe Daniel Ogochukwu, API Popoola and Abraham A Adeleke. “Characterization of copper smelter dust for copper recovery”. Procedia Manufacturing 7 (2017): 121-126.
6. Okanigbe DO, API Popoola and AA Adeleke. “Hydrometallurgical processing of copper smelter dust for copper recovery as nano-particles: A review”. Energy Technology (2017): 205-226.
7. Okanigbe Daniel., et al. “Centrifugal separation experimentation and optimum predictive model development for copper recovery from waste copper smelter dust”. Cogent Engineering 5.1 (2018): 1551175.
8. Flores Gerardo Alvear, Carlos Risopatron and Joe Pease. “Processing of complex materials in the copper industry: challenges and opportunities ahead”. Jom 72.10 (2020): 3447-3461.
9. Okanigbe DO, API Popoola and AA Adeleke. “Thermal analysis and kinetics of the oxidative roasting process of a copper smelter dust”. The International Journal of Advanced Manufacturing Technology 94.5 (2018): 2393-2400.
10. Moldabayeva GZ., et al. “Electrosmelting of lead-containing dusts from copper smelters”. Journal of Sustainable Metallurgy 1.4 (2015): 286-296.
11. Priya Jayati., et al. “High-purity copper recycled from smelter dust by sulfation roasting, water leaching and electrorefining”. Environmental Chemistry Letters 18.6 (2020): 2133-2139.
12. Gorai Bipra, Ranajit Kumar Jana and Zahid Husain Khan. “Electrorefining electrolyte from copper plant dust”. Materials Transactions 43.3 (2002): 532-536.
13. Ha Tae Kyung., et al. “Selective leaching and recovery of bismuth as Bi2O3 from copper smelter converter dust”. Separation and Purification Technology 142 (2015): 116-122.
14. Qiang Li, Isabel SS Pinto and Zhao Youcai. “Sequential stepwise recovery of selected metals from flue dusts of secondary copper smelting”. Journal of cleaner production 84 (2014): 663-670.
15. Vítková Martina., et al. “Leaching of metals from copper smelter flue dust (Mufulira, Zambian Copperbelt)”. Applied Geochemistry 26 (2011): S263-S266.
16. Bakhtiari F., et al. “Bioleaching of copper from smelter dust in a series of airlift bioreactors”. Hydrometallurgy 90.1 (2008): 40-45.
17. Vakylabad, Ali Behrad. “A comparison of bioleaching ability of mesophilic and moderately thermophilic culture on copper bioleaching from flotation concentrate and smelter dust”. International journal of mineral processing 101.1-4 (2011): 94-99.
18. Vakylabad Ali Behrad., et al. “Bio-processing of copper from combined smelter dust and flotation concentrate: A comparative study on the stirred tank and airlift reactors”. Journal of hazardous materials 241 (2012): 197-206.
19. Morales A., et al. “Treatment of copper flash smelter flue dusts for copper and zinc extraction and arsenic stabilization”. Hydrometallurgy, 105(1-2) (2010): 148-154.
20. Montenegro Victor, Hiroyuki Sano, and Toshiharu Fujisawa. “Recirculation of Chilean copper smelting dust with high arsenic content to the smelting process”. Materials transactions 49.9 (2008): 2112-2118.
21. Alguacil Francisco Jose., et al. “Recycling of copper flue dust via leaching-solvent extraction processing”. Desalination and Water Treatment 56.5 (2015): 1202-1207.
22. Font Oriol., et al. “Copper flash smelting flue dust as a source of germanium”. Waste and biomass valorization (2017).
23. Okanigbe Daniel O, Abimbola PI Popoola and Abraham A Adeleke. “Enhanced Recycling of Waste Copper Smelter Dust from Exist-

ing and Proposed Smelter Plant at the Palabora Copper (pty) ltd, impopo, South Africa". IOP Conference Series: Materials Science and Engineering. IOP Publishing 391 (2018): 1.

24. Adeleke AA., et al. "Experimentation, Modeling, and Optimum Conditions of Pyro-Hydrometallurgical-Precipitation Reaction Technology for Recovery of Copper as Oxide of Nanoparticles from a Copper Dust". Energy Technology 2020: Recycling, Carbon Dioxide Management, and Other Technologies. Springer, Cham (2020): 189-201.
25. Chu Yingying., et al. "Micro-copper powders recovered from waste printed circuit boards by electrolysis". Hydrometallurgy 156 (2015): 152-157.
26. Cook Benjamin S., et al. "Inkjet catalyst printing and electroless copper deposition for low-cost patterned microwave passive devices on paper". Electronic Materials Letters 9.5 (2013): 669-676.
27. Bakhtiari Fereshteh. "Synthesis and characterization of tenorite (CuO) nanoparticles from smelting furnace dust (SFD)". Journal of mining and metallurgy, section B: Metallurgy 49.1 (2013): 21-21.
28. Gawande Manoj B., et al. "Cu and Cu-based nanoparticles: synthesis and applications in catalysis". Chemical reviews 116.6 (2016): 3722-3811.
29. Jones John-Paul, GK Surya Prakash and George A Olah. "Electrochemical CO2 reduction: recent advances and current trends". Israel Journal of Chemistry 54.10 (2014): 1451-1466.
30. Xie Huan., et al. "Cu-based nanocatalysts for electrochemical reduction of CO2". Nano Today 21 (2018): 41-54.
31. Ingle Avinash P, Nelson Duran and Mahendra Rai. "Bioactivity, mechanism of action, and cytotoxicity of copper-based nanoparticles: a review". Applied microbiology and biotechnology 98.3 (2014): 1001-1009.
32. Ameh Thelma and Christie M Sayes. "The potential exposure and hazards of copper nanoparticles: A review". Environmental Toxicology and Pharmacology 71 (2019): 103220.
33. Ogunsona Emmanuel O., et al. "Engineered nanomaterials for antimicrobial applications: A review". Applied Materials Today 18 (2020): 100473.
34. Foley Jonathan A., et al. "Solutions for a cultivated planet". Nature 478.7369 (2011): 337-342.
35. Mueller Nathaniel D., et al. "Closing yield gaps through nutrient and water management". Nature 490.7419 (2012): 254-257.
36. Li Peng, et al. "Eco-friendly biomolecule-nanomaterial hybrids as next-generation agrochemicals for topical delivery". EcoMat 3.5 (2021): e12132.
37. Guan Xiangyu., et al. "CuO nanoparticles alter the rhizospheric bacterial community and local nitrogen cycling for wheat grown in a calcareous soil". Environmental science & technology 54.14 (2020): 8699-8709.
38. Camara Marcela Candido., et al. "Development of stimuli-responsive nano-based pesticides: emerging opportunities for agriculture". Journal of nanobiotechnology 17.1 (2019): 1-19.
39. Ngo Quoc Buu., et al. "Effects of nanocrystalline powders (Fe, Co and Cu) on the germination, growth, crop yield and product quality of soybean (Vietnamese species DT-51)". Advances in Natural Sciences: Nanoscience and Nanotechnology 5.1 (2014): 015016.
40. CO Dimpka., et al. "Bioactivity and biomodification of Ag, ZnO, CuO nanoparticles with relevance to plant performance in agriculture". IndBiotechnol 8 (2012): 344-357.
41. Tamilvanan A, K Balamurugan and M Vijayakumar. "Effects of nano-copper additive on performance, combustion and emission characteristics of Calophylluminophyllum biodiesel in CI engine". Journal of Thermal Analysis and Calorimetry 136.1 (2019): 317-330.
42. Lee Youngil., et al. "Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics". Nanotechnology 19.41 (2008): 415604.
43. Conway Jon R., et al. "Aggregation, dissolution, and transformation of copper nanoparticles in natural waters". Environmental science & technology 49.5 (2015): 2749-2756.
44. Adeleye Adeyemi S., et al. "Influence of extracellular polymeric substances on the long-term fate, dissolution, and speciation of copper-based nanoparticles". Environmental science & technology 48.21 (2014): 12561-12568.
45. Slotte Martin and Ron Zevenhoven. "Energy requirements and life cycle assessment of production and product integration of silver, copper and zinc nanoparticles". Journal of Cleaner Production 148 (2017): 948-957.

46. Li T., et al. “Concentrations and solubility of trace elements in fine particles at a mountain site, southern China: regional sources and cloud processing”. Atmospheric Chemistry and Physics 15.15 (2015): 8987-9002.
47. Xu Bin., et al. “A review of the comprehensive recovery of valuable elements from copper smelting open-circuit dust and arsenic treatment”. Jom 72.11 (2020): 3860-3875.
48. Bakhtiari F., et al. “Continuous copper recovery from a smelter’s dust in stirred tank reactors”. International journal of mineral processing 86.1-4 (2008): 50-57.
49. Chen Ya., et al. “Recovery of bismuth and arsenic from copper smelter flue dusts after copper and zinc extraction”. Minerals Engineering 39 (2012): 23-28.
50. Guo Xueyi., et al. “Separation and recovery of arsenic from arsenic-bearing dust”. Journal of environmental chemical engineering 3.3 (2015): 2236-2242.
51. Zhang Rong-Liang., et al. “Treatment process of dust from flash smelting furnace at copper smelter by oxidative leaching and dearsenifying process from leaching solution”. Zhongnan DaxueXuebao (ZiranKexue Ban)/Journal of Central South University(-Science and Technology) 37.1 (2006): 73-78.
52. Jia YF., et al. “Preparation, Characterization and Solubilities of Adsorbed and Co-Precipitated Iron (III)-Arsenate Solids”. Electrometallurgy and Environmental Hydrometallurgy 2 (2003): 1923-1935.
53. Shibayama Atsushi., et al. “Treatment of smelting residue for arsenic removal and recovery of copper using pyro–hydrometallurgical process”. Journal of hazardous materials 181.1-3 (2010): 1016-1023.
54. Pérez-Moreno SM., et al. “Diagnose for valorisation of reprocessed slag cleaning furnace flue dust from copper smelting”. Journal of Cleaner Production 194 (2018): 383-395.
55. Yuan Gao-Qing., et al. “Shape-and size-controlled electrochemical synthesis of cupric oxide nanocrystals”. Journal of Crystal Growth 303.2 (2007): 400-406.
56. Neupane Madhav Prasad., et al. “Temperature driven morphological changes of hydrothermally prepared copper oxide nanoparticles”. Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films 41.3 (2009): 259-263.
57. Outokesh M., et al. 2011. “Hydrothermal synthesis of CuO nanoparticles: study on effects of operational conditions on yield, purity, and size of the nanoparticles”. Industrial & engineering chemistry research, 50(6), pp.3540-3554.
58. Zhu Junwu., et al. “Highly dispersed CuO nanoparticles prepared by a novel quick-precipitation method”. Materials Letters 58.26 (2004): 3324-3327.
59. Nikam Arun V., et al. “pH-dependent single-step rapid synthesis of CuO and Cu2O nanoparticles from the same precursor”. Crystal Growth & Design 14.9 (2014): 4329-4334.
60. Vidyasagar CC., et al. “Solid-state synthesis and effect of temperature on optical properties of Cu–ZnO, Cu–CdO and CuO nanoparticles”. Powder technology 214.3 (2011): 337-343.
61. Baláž Matej., et al. “Synthesis of copper nanoparticles from refractory sulfides using a semi-industrial mechanochemical approach”. Advanced Powder Technology 31.2 (2020): 782-791.
62. Gupta Kalyani, Marco Bersani and Jawwad A Darr. “Highly efficient electro-reduction of CO2 to formic acid by nano-copper”. Journal of Materials Chemistry 4.36 (2016): 13786-13794.
63. Elouali Sofia., et al. “Gas sensing with nano-indium oxides (In2O3) prepared via continuous hydrothermal flow synthesis”. Langmuir 28.3 (2012): 1879-1885.
64. Seredkin Maxim, Alexander Zabolotsky and Graham Jeffress. “In situ recovery, an alternative to conventional methods of mining: Exploration, resource estimation, environmental issues, project evaluation and economics”. Ore Geology Reviews 79 (2016): 500-514.
65. Pappu Asokan, Mohini Saxena and Shyam R Asolekar. “Solid wastes generation in India and their recycling potential in building materials”. Building and environment 42.6 (2007): 2311-2320.
66. Hazra Tumpa and Sudha Goel. “Solid waste management in Kolkata, India: Practices and challenges”. Waste management 29.1 (2009): 470-478.

67. Hudson-Edwards., et al. “Mine wastes: past, present, future”. Elements 7.6 (2011): 375-380.
68. Martens Evelien., et al. “Toward a more sustainable mining future with electrokinetic in situ leaching”. Science Advances 7.18 (2021): eabf9971.
69. Okanigbe Daniel Ogochukwu. “Production of copper and copper oxide nano-particles from leach solution of low grade copper smelter dust”. (2019).
70. Crane RA and DJ Sapsford. “Selective formation of copper nanoparticles from acid mine drainage using nanoscale zerovalent iron particles”. Journal of hazardous materials 347 (2018): 252-265.
71. Stefanowicz T, Osińska M and Napieralska-Zagozda S. “Copper recovery by the cementation method”. Hydrometallurgy 47.1 (1997): 69-90.
72. Gauteng Scrap Metal Prices - South Africa.
73. Alibaba.com.
74. Crane RA and DJ Sapsford. “Towards “Precision Mining” of wastewater: Selective recovery of Cu from acid mine drainage onto diatomite supported nanoscale zerovalent iron particles”. Chemosphere 202 (2018): 339-348.
75. Borglin Sharon E, George J Moridis and Curtis M Oldenburg. “Experimental studies of the flow of ferrofluid in porous media”. Transport in porous media 41.1 (2000): 61-80.
76. Nicol Michael J and Zaimawati Zainol. “The development of a resin-in-pulp process for the recovery of nickel and cobalt from laterite leach slurries”. International Journal of Mineral Processing 72.1-4 (2003): 407-415.
77. Udayar T, MH Kotze and V Yahorava. “Recovery of uranium from dense slurries via resin-in-pulp”. Proceedings of the 6th Southern African Base Metals Conference (2011).