Chapter 2 Resource Recovery and Recycling from Waste Metal Dust (II): Waste Copper Dust



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2.1 Introduction

The complex process [1] of extracting copper from mineral resources [2] is shown in Fig. 2.1.

These mineral deposits create mineralization zones that are commercially advantageous to the miner. As a result, several mining techniques are employed to explore and make use of them for their copper values [3]. Unit operations are performed before, during, and after the mining process [4], and they normally take place on a facility and are done directly to speed up the mining process [5]. These activities before, during, and after mining frequently produce desired items as well as undesirable by-products [6], such as waste copper dusts (WCD).

WCD produced by copper mining operations is currently inevitable [7], and if not appropriately controlled, they constitute a risk to human health and the environment [7-11].

When metal ore is chemically heated, dangerous gases are created, and WCD are frequently composed of copper and other metal values close to these gases [12, 13]. These composites are usually categorized as dangerous under South Africa (SA) legislation due to their poisonous ingredients (Fig. 2.2).

Adhering to this legislation often presents a challenge, because most copper mining businesses work on a linear economic model, which is rather straightforward because it is based on extracting mineral resources and converting them into a product that eventually becomes waste (i.e., "taking, manufacturing, and wasting")

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Fig. 2.1 Flowchart of the copper mining process. (Source: Google image)



Fig. 2.2 Characterization, content, and SA legislation on WCD [14]



Fig. 2.3 South Africa's copper mine production in metric tons from 2011 to 2018. (Image courtesy of Google)

[15–17]. This economic model is distinct from the circularity model, which contains ideas like "resource recovery and recycling; a system that minimizes the use of resource inputs that result in waste, pollution, and carbon emissions [17, 18]."

Given the aforementioned, Evert Swanepoel, the executive chairperson of the Copper Development Association of Africa (CDAA), stated in a report from Mandarin Finance and Economics [19] that "Due to the declining and limited domestic copper production (Fig. 2.3), SA is expected to prioritize the recycling of copper resources to ensure there remains sufficient stock as the economy becomes more energy efficient and less dependent on fossil fuels" [20, 21]. Two-thirds of all copper ever produced is still in use today, the CDAA chairman continued. Nevertheless, he noted that only Palabora Mining Company was still in operation to provide domestic demand in SA, where copper was becoming increasingly rare [22]. According to the CDAA chairman, the mine was on the verge of closing down [23], while explorer and developer Orion Minerals is constructing a new copper mine in the town of Prieska in the Northern Cape [24]. Ultimately, this project will not be finished until 2023.

Furthermore, exporting a lot of copper scrap to foreign recyclers limits the amount of domestic copper available, giving local recyclers less supplies of copper scrap to work with. This leaves the nation with the options of "using recycled copper or importing copper raw material?"

Therefore, it is noteworthy at this moment to conduct research into resource recovery and recycling from waste metal dust (WCD) [25–29]. In fact, as a result of these efforts, the circularity model is given a powerful voice in the copper mining industry. This approach closes the copper loop while also helping to lessen adverse environmental consequences.

This chapter will explore the generation, description, and recirculation of WCD, as well as resource recovery and recycling from WCD, in light of this line of thinking. Following that, a list of suggested research fields for turning the South African WCD into a useful resource follows.

2.2 Waste Copper Dust

2.2.1 Generation

Impurities must be removed in copper metallurgy in order to produce copper that is of a high quality [30, 31], but they must also be removed for environmental reasons [32]. It is reasonable to anticipate an even more dire situation in the future given the continuous rise in impurities in copper ore over time [33]. Impurities must be kept below the limits permitted by national and international regulations for the copper industry [34], and the overall emission of hazardous substances must be reduced.

Oxidation, slagging, and volatilization are used to remove impurities from copper during the smelting, conversion, and refining processes [35, 36]. The Teniente Converter, Inco Flash, Outokumpu Flash, and Mitsubishi processes, among others, have all seen advancements thanks to a mix of intensive reactors that use oxygen or oxygen-enriched air as the blowing gas. The way of removing impurities, however, has remained unchanged and has instead turned into a significant constraint in the contemporary method of copper smelting and conversion [37, 38].

Gaseous emissions generated from copper processing include heavy metals, water vapor, SO₂, N₂, and O₂ in addition to other contaminants [39]. As a result of the gas cleaning procedure, WCD is produced [40]. WCD contains condensate matter and small semi-melted concentrate particles that are carried with the off-gas.

2.2.2 Description of WCD

2.2.2.1 Particle Size Distribution of WCD

The WCD is primarily made up of fine-grained particles, according to the WCD production mechanism and the results of characterizing the WCD for its particle size distribution. The following researchers: Okanigbe et al. [25], Ha et al. [41], Bakhtiari et al. [42, 43], Vakylabad et al. [44], Morales et al. [45], Balladares et al. [46], and Xu et al. [47] shared that the majority of the particles, measured quantitatively, are very small and lie within the size range of 5–50 μ m below the 53- μ m sieve aperture. When Okanigbe, [48], studied the South African WCD's –53 μ m size fraction using the laser diffraction technique, the results showed that the bulk particle sizes in this size fraction were primarily between 24 and 30 μ m, with no particles falling within the nano-small range (Table 2.1). This knowledge was helpful, especially for the actual separation of the South African WCD [27].

Size (µm)	%Change	%Passing	Size (µm)	%Change	%Passing
2000.00000	0.00	100.00	4.63000	1.21	3.88
1674.00000	0.00	100.00	3.39000	0.93	2.67
1408.00000	0.00	100.00	3.27000	0.71	1.74
1184.00000	0.00	100.00	2.75000	0.54	1.03
995.60000	0.00	100.00	2.31300	0.38	0.49
837.20000	0.00	100.00	1.94500	0.11	0.11
704.00000	0.00	100.00	1.53500	0.00	0.00
592.00000	0.00	100.00	1.37500	0.00	0.00
497.30000	0.00	100.00	1.15600	0.00	0.00
418.60000	0.00	100.00	0.97200	0.00	0.00
352.00000	0.00	100.00	0.81800	0.00	0.00
296.00000	0.34	100.00	0.68800	0.00	0.00
248.90000	0.44	99.66	0.57800	0.00	0.00
209.30000	0.57	99.22	0.48500	0.00	0.00
176.00000	0.72	98.65	0.40900	0.00	0.00
148.00000	0.90	97.93	0.34400	0.00	0.00
124.60000	1.16	97.03	0.28900	0.00	0.00
104.70000	1.53	95.37	0.24300	0.00	0.00
88.00000	2.07	94.34	0.20400	0.00	0.00
74.00000	2.87	92.27	0.17200	0.00	0.00
62.23000	3.92	89.40	0.13500	0.00	0.00
52.33000	5.12	85.43	0.12200	0.00	0.00
44.00000	6.29	80.36	0.10200	0.00	0.00
37.00000	7.30	74.07	0.08600	0.00	0.00
31.11000	8.09	66.77	0.07200	0.00	0.00
26.16000	8.57	58.63	0.06100	0.00	0.00
22.00000	8.63	50.11	0.05100	0.00	0.00
18.50000	8.28	41.43	0.04300	0.00	0.00
15.56000	7.33	33.20	0.03600	0.00	0.00
13.03000	6.14	25.37	0.03000	0.00	0.00
11.00000	4.98	19.73	0.02550	0.00	0.00
9.25000	3.96	14.75	0.02150	0.00	0.00
7.73000	3.06	10.79	0.01810	0.00	0.00
6.59000	2.26	7.73	0.01520	0.00	0.00
5.50000	1.59	5.47	0.01280	0.00	0.00

 Table 2.1
 PSD of WCD as Determined with the Laser Diffraction [48]

	Content (wt. %)								
Composition	WCD 1	WCD 2	WCD 3	WCD 4	WCD 5	WCD 6	WCD 7		
Cu	18.02	10.8	10.90	27.00	7.53	41.70	4.00		
Fe	13.36	0.8	1.60	11.00	-	29.60			
Zn	0.27	15.6	7.80	5.8	40.21	0.30	18.00		
S	3.44	10.4	-	7.5	-	13.00	7.00		
Bi	0.02	3.5	1.90	0.20	-	2.30	1.10		
As	-	19.4	7.10	13.0	-	0.40	20.5		
Ca	3.52	-	-	-	-	-	-		
Mg	2.86	-	-	-	-	-	-		
Ti	1.11	-	-	-	-	-	-		
Si	33.06	-	-	-	-	-	-		
Al	22.19	-	-	-	-	-	-		
Cd	-	-	1.30	-	-	-	9.50		
Pd	0.12	7.80	14.20	1.50	6.62	0.00	8.00		
Sb	-	0.1	0.10	-	-	-	1.20		
Others	1.95	31.6	55.10	33.80	45.64	12.4	-		

Table 2.2 Different chemical compositions of WCD

Key: WCD 1 = Okanigbe et al. [25]; WCD 2 = Montenegro et al. [39]; WCD 3 = Ha et al. [41]; WCD 4 = Morales et al. [45]; WCD 5 = Qiang et al. [49]; WCD 6 = Vítková et al. [50]; WCD 7 = Font et al. [51].

2.2.2.2 Chemical Composition of Typical WSD

According to Table 2.2, the composition of this WCD varies depending on the operation. The mineralogy of the concentrates, fluxes, and circulating material (slag, WCD, etc.), as well as their corresponding proportions, determines the composition [46], while the type of reactor used in the smelting and conversion procedures mostly affects the mass of WCD produced [47].

As shown in Table 2.2, WCD typically contains the minor elements copper (Cu), iron (Fe), lead (Pb), arsenic (As), cadmium (Cd), antimony (Sb), zinc (Zn), bismuth (Bi), and selenium (Se), but the exact form of each element depends on the environmental factors and operational parameters of the smelting and converting processes [39]. The ratio of these components in the WCD aids in determining the best waste management approach (i.e., disposal, recirculation, resource recovery, and recycling) to use.

2.2.2.3 Mineralogy of WCD

Researchers Vakylabad et al. [44, 52], Morales et al. [45], Qiang et al. [49], Vtková et al. [50], Font et al. [51], Alguacil et al. [53], Ettler et al. [54], and Xu et al. [55] examined the phase structures of the WCD. The phases that are frequently found in WCD are represented in Table 2.3 and mostly consist of complex copper oxides and sulfides, although the compositions of these WCD vary greatly (Table 2.3).

	Phases							
Composition	WCD 1	WCD 2	WCD 3	WCD 4				
Cu	Cu _{6.88} Fe _{17.12} O _{32.00}	CuO	CuSO _{4.00} .5H _{2.00} O, CuFeO _{2.00}	CuSO _{4.00} , CuS				
	$Cu_{4.00}Fe_{4.00}S_{32.00}$							
Fe	$Mg_{0.04}Fe_{2.96}O_{4.00}$	-	Fe _{3.00} O _{4.00}	-				
Zn	-	ZnO	-	ZnS, ZnSO _{4.00}				
Ca	Ca(SO _{4.00})(H _{2.00} O) _{2.00}							
Pb	-	PbO	-	PbSO _{4.00}				
As	-	-	-	As _{2.00} O _{3.00}				
Al	Al(Al _{0.69} Si _{1.22} O _{4.85})	AlCl _{3.00}	-	-				
Si	SiO _{2.00}	-	-	-				

Table 2.3 Mineralogy of different WCD

Key: WCD 1 = Okanigbe et al. [25]; WCD 2 = Qiang et al. [49]; WCD 3 = Vítková et al. [50]; WCD 4 = Font et al. [51]



Elements		Spectrums										
		4		5		6		7	Ave	rage	35	
	Wt%	σ	Wt%	σ	Wt%	σ	Wt%	σ	≈Wt%	≈đ	30	 +W12%
Cu	31.0	0.3	4.7	0.2	30.2	2.0	37.5	0.3	25.9	0.7	E 23	
Fe	39.4	0.3	14.3	0.2	7.4	1.4	13.9	0.2	18.8	0.5	8 20	
0	23.3	0.3	40.7	0.3	36.2	1.8	30.4	0.2	32.7	0.7	8 15	
Ca	3.2	0.1	6.7	0.1	14.3	4	1.3	0.1	3.7	0.1		
AI	1.2	0.1	15.2	0.1	13.2	1.0	5.3	0.1	8.7	0.3	€ 10	
Si	1.0	0.1	15.0	0.1	12.9	1.1	4.7	0.1	8.4	0.4	3	
5	0.4	0.0	0.7	0.0		•	3.3	0.1	1.5	0.0	. BLLLLL . a.a.	
ТЪ	0.4	0.4	0.0	0.3		-	-	· · ·	0.2	0.4	Cu Fe O Ca Al Si S Tb K Ti Zn	
к	12	-	1.4	0.1	14	-	1.3	0.0	1.4	0.0	Elements	
Ti	1		1.2	0.1	1.1		1.3	0.1	1.3	0.1		
Zn			•		1.0		1.0	0.2	1.0	0.2		

Fig. 2.4 Scanning electron micrograph and energy dispersive spectrums of WCD from South Africa

2.2.2.4 Morphology of WCD

SEM images and energy dispersive spectra of a WCD from SA are shown in Fig. 2.4. Few unevenly shaped particles can be seen in the micrographs, whereas most particles are typically spherical in shape [25, 47]. The appearance of the WCD under the electron microscope is typical of semi-molten or molten material solidified by cooling in a gas transport system [25], as agreed upon by various researchers [25, 47], as opposed to particles reacting in the solid state, which have a more angular look [46]. The diameters of the particles, which range from submicron to micron, and their adhesion to one another [25] can also be seen in Fig. 2.4.

2.2.3 Recirculation of WCD

The approach of recycling the WCD back into the furnaces, according to Bakhtiari et al. [43], decreases their efficacy and raises the amount of energy needed for smelting; additionally, due to its characteristically fine nature, $5-50 \mu m$ [25, 41, 47], it damages the refractory bricks when returned to the furnace and places a circular load on the furnaces.

To determine the impact of WCD recirculating in the smelting process on WCD generation and the behavior of certain impurities among the matte and slag phases, Montenegro et al. [39] tested this recirculation strategy at the laboratory scale. The authors claim that copper can be successfully recovered using WCD recirculation. Recirculation into the smelting process can reduce WCD generation if the carry-over of recirculated WCD is successfully reduced. However, the ultimate matte quality determines how much WCD recirculation occurs.

Additionally, the recirculation of WCD into the smelting process will be prevented by exceptionally high As concentrations and higher concentrations of other impurities including Bi, Pb, and Sb [39, 56]. This is because recirculation causes the distributions of these contaminants in matte to dramatically rise. Therefore, the way those contaminants behave may restrict how much WCD recirculation occurs during the process.

2.2.4 Resource Recovery and Recycling from WCD

2.2.4.1 The Recovery of Metals from WCD

It is common for one or more extractive metallurgy unit activities to be combined in order to recover metal values from WCD. Following is a discussion of the various extractive metallurgy and mineral processing unit activities for the recovery of these metal values:

The Use of Hydrometallurgical Techniques

The work by Li et al. [57] showed how arsenic was removed from the WCD leach solution by co-precipitation with ferric ions. Secondary products from WCD, are abundant in bismuth (Bi) and other significant metals, claim Ha et al. [41]. They provided a cost-effective hydrometallurgical method for extracting Bi from WCD in their paper. When used as leaching reagents, a solution of H_2SO_4 and NaCl can effectively remove Bi from WCD. Under ideal circumstances, a 92% leaching efficiency was attained. Guo et al. [58] created a hydrometallurgical procedure to selectively recover arsenic from WCD by leaching the WCD with NaOH-Na₂S.

The Use of Bio-Hydrometallurgy Techniques

The bioleaching of WCD from smelters in Iran's Sarcheshmeh copper complex was studied by Bakhtiari et al. [43]. Although sulfide minerals, notably pyrite, in copper concentrates undergo oxidation processes that release acid, authors reported that the WCD bio-treatment process consumes acid. A different study by Bakhtiari et al. [42] looked at the bioleaching of copper from the WCD of the Sarcheshmeh copper smelting plant. 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.

The Use of Pyrometallurgical-Hydrometallurgical Techniques

The recovery of precious metals and the removal of arsenic from WCD have both been extensively investigated using the pyro-hydrometallurgical method [47].

The Use of Physical Separation Techniques

The process parameterization of a centrifugal concentrator for the separation of a WCD was followed by a theoretical contribution including the creation of a system of predictive models in the work by Okanigbe et al. [27]. According to the findings, a maximum grade of approximately 35.02 wt% Cu was attained at 120G for the rotational bowl speed, 3.0 L/min for the water flow rate, 1.48 L/min for the continuous experimental flow rate, and 0.5 L/min for the liquid to solid ratio. Similar to this, under the same testing conditions, a minimum output of 14.58% SiO₂ and 10.29% Al₂O₃ was attained. This clearly shows a trend toward ideal experimental settings designed to maximize Cu output and reduce SiO₂ and Al₂O₃ levels.

Using unit operations of zinc vapor evaporation and condensation as well as super-gravity separation of copper droplets, researchers from Gao et al. [59] suggested a novel method to efficiently extract metallic copper and crown zinc from WCD.

Stabilization/Solidification

Most of WCD are considered as hazardous pollutants because they contain lots of heavy metals; consequently, several researchers have focused on the stabilization/ solidification of them [45, 60–62]. Furthermore, since As_2O_3 is abundant worldwide, it is not practical from an economic standpoint to entirely recycle As-rich WCD from non-ferrous metallurgies [63]. Should WCD not meet the conditions set forth by the European Union (EU) for landfilling in hazardous waste disposal sites (Table 2.2), it must be solidified or stabilized before it can be accepted at any land-fill site.

Conversion of WCD into Value-Added Product

With the shortage of mineral resources, direct disposal after stabilization/solidification processes might not be the best methods for treating WCD like the one generated in SA.

Granted the WCD from SA has the bare minimum As, Bi, Pb, and Sb contents necessary for landfilling in hazardous waste disposal facilities. The best way to manage this waste is through resource recovery and recycling by conversion into useful commodities for additional value.

Hence, the following research suggestions on transforming WCD from SA into a value-added product are listed below, these ideas have been made public in their whole forms:

- 1. Thermal and Mechanical Properties (I): Optimum Predictive Thermal Conduction Model Development for Epoxy Filled Copper Oxide Nanoparticles Composite Coatings on Spent Nuclear Fuel Steel Casks.
- 2. Thermal and Mechanical Properties (I): Spark Plasma Sintered Ti–6Al–4V Alloy Reinforced with Mullite-Rich-tailings for Production of Energy Efficient Brake Rotor.
- 3. Wave Energy Converter Design: Seawater Integrity and Durability of Epoxy-Resin Filled Corrosive Microorganism Surface Modified Waste Copper Dust.
- 4. Aircraft Engine Fan Blade Design: Impact Tolerance Prediction of Partially Filled 3D Printed Aluminum, Titanium, and PEEK Filled Waste Copper Dust.
- 5. Preparation and Characterization of Hydrotalcite-Derived Material from Mullite-Rich-Tailings (I): Transesterification of Used Cooking Oil to Biodiesel.
- 6. Preparation and Characterization of Hydrotalcite-Derived Material from Mullite-Rich-Tailings (II): CO₂ Capture from Coal-Fired Thermal Power Plants.

2.3 Conclusions

Discussions on the production, description, and recirculation of WCD, as well as resource recovery and recycling from South Africa's WCD, were given in this chapter and arrived at the following deductions:

- 1. As a result of the gas cleaning procedure, WCD is produced.
- The bulk particles in the South African WCD's -53 μm size fraction were primarily made up of 24–30 μm particle sizes.
- 3. Because of the chemical makeup and/or mineralogy of some WCD, recirculation has been deemed unacceptable.
- 4. The WCD from SA contains the minimal minimum amount of As, Bi, Pb, and Sb required for landfilling at facilities for the disposal of hazardous waste.

Therefore, it was suggested that the adoption of creative ideas that aim to transform WCD into functional material rather than recirculation or disposal will help to reduce adverse environmental consequences while also closing the copper loop (Zero-waste production).

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