

The potential for copper slag waste as a resource for a circular economy: A review – Part II

Tina Chanda Phiri, Pritam Singh, Aleksandar N. Nikoloski *

Murdoch University, Faculty of Energy and Engineering, 90 South Street, Murdoch WA, Australia

ARTICLE INFO

Keywords:

Copper slag waste
Circular economy
Characterisation
Metal recovery
Utilisation

ABSTRACT

Copper slag waste has continued to cause increasing concerns due to the huge volumes being produced annually worldwide. This paper presents a review of copper slag as a potential resource for cobalt and copper metals for a circular economy. An overview of the chemical and mineralogical characterisation of copper slag from 21 major producing countries is discussed. Characterisation is an important consideration in understanding the nature and environmental behaviour of copper slag. Copper smelter slags are highly heterogeneous and chemically diverse. The principal slag constituents are silica, ferrous oxide, ferric oxide, limestone, and alumina. The slag also contains high concentrations of valuable metals and metalloids such as copper, cobalt, zinc, calcium, aluminium, silver, magnesium, and lead. The variation in the chemical and mineralogical composition of copper slag is mainly influenced by the type of concentrate, type of fluxes, furnace type and cooling rates during and following the smelting and converting processes. Furthermore, the various processing strategies for metal recovery, such as flotation, pyrometallurgy and hydrometallurgy is presented. Finally, utilisation of the copper slag waste in the concrete industry to promote environmental sustainability is discussed. This review demonstrates that processing and repurposing of copper slag waste has benefits of a circular economy such as increasing critical metal supply, lowering the cost of concrete, and reducing environmental harm.

1. Introduction

Copper slag is a waste produced during pyrometallurgical processing of metals from copper concentrates. The decomposition and oxidation reactions of the sulphide minerals in the concentrate leads to the production of three separate phases: matte, slag, and an off-gas. The slag phase consists predominantly of silica (SiO_2), ferrous oxide (FeO), ferric oxide (Fe_2O_3), and small amounts of calcia (CaO), and alumina (Al_2O_3) as well as metals such as copper (Cu), cobalt (Co), silver (Ag), nickel (Ni), zinc (Zn), lead (Pb), cadmium (Cd), and iron (Fe) in oxide, or sulphide and/or metallic forms. It is estimated that for every ton of copper produced, about 2.2 ton of slag is generated (Gorai et al., 2003) and approximately, 37.7 million tons is produced annually worldwide. The disposal of these huge quantities of copper slag require large areas of land which presents waste management problems (Gorai et al., 2003; Alp et al., 2008; Al-Jabri et al., 2011; Roy et al., 2015; Potysz et al., 2015). Copper slag waste contains toxic heavy metals such as Pd, Cd, As, Cu, and Zn which may be a source of pollution affecting surface water, soil and groundwater (Parsons et al., 2001; Lottermoser, 2002; Ettler

et al., 2009; Piatak et al., 2014; Potysz et al., 2018). The discharge of these heavy metals poses serious threats to all living organisms (Kambole et al., 2019). Therefore, it is increasingly necessary to reduce waste disposal by extraction of valuable metals from the slag waste in a circular economy. A circular economy involves sustainable processing strategies of 'produce, use and recycle' (Nikoloski, 2020). It unlocks opportunities for production of metals for energy storage using cleaner and more efficient production technologies as well as developing effective recycling strategies to solve both the metal supply and waste disposal problems. Copper slag contains significant amounts of valuable metals with average of 1.83 wt% Zn, 1.67 wt% Ag, 1.36 wt% Mg, 1.19 wt% Cu, 0.94 wt% Pb, and 0.48 wt% Co (Table 3). This has attracted increasing interest to recover these valuable metals from copper slag using various techniques such as flotation, hydrometallurgy, pyrometallurgy, and an integration of pyrometallurgy and hydrometallurgy. Furthermore, copper slag is reported to possess favourable physical and mechanical properties such as abrasion resistance and high stability (Gorai et al., 2003). This has attracted interest for production of blended cements, pavement, abrasives, concrete, tiles, glass, cutting tools, and

* Corresponding author.

E-mail address: a.nikoloski@murdoch.edu.au (A.N. Nikoloski).

<https://doi.org/10.1016/j.mineng.2021.107150>

Received 3 February 2021; Received in revised form 28 July 2021; Accepted 17 August 2021

Available online 26 August 2021

0892-6875/Crown Copyright © 2021 Published by Elsevier Ltd. All rights reserved.

Table 1

The average chemistry of copper smelter slag from 21 countries covering over 80 studies.

Wt%	Australia	Canada	Chile	China	Congo	Finland	Italy	India	Iran	Kaza- khstan	Mexico	Namibia	Poland	Serbia	Singa- pore	Spain	South Africa	South Korea	Turkey	USA	Zambia
Al ₂ O ₃	4.00	–	–	3.71	6.00	–	6.29	2.26	9.16	–	7.30	4.70	11.70	3.78	–	6.71	2.00	4.45	2.95	11.93	7.20
CaO	13.37	–	0.90	1.80	8.60	–	12.12	2.90	6.29	–	1.66	4.50	13.38	6.00	–	5.18	2.00	2.85	2.33	11.66	10.07
Fe	–	34.66	40.26	37.26	23.85	40.90	42.65	45.10	44.78	30.00	37.89	32.47	31.25	39.09	38.05	45.54*	–	48.55	45.50	38.81	23.80
FeO	36.09	–	–	39.85	–	–	–	28.16	–	–	–	9.49	–	33.80	–	45.54	–	–	–	–	–
Fe ₂ O ₃	–	–	3.95	–	–	–	54.17	58.05	29.68	–	–	32.47	23.96	9.39	–	12.73	–	–	51.00	43.90	–
K ₂ O	0.40	–	–	–	–	–	1.33	0.75	3.77	–	1.06	0.30	3.52	–	–	1.21	–	–	0.50	1.36	2.54
MgO	1.16	–	0.84	1.51	5.60	–	1.95	1.68	1.94	–	1.29	1.43	3.65	1.66	–	1.10	1.00	1.55	2.82	1.85	3.31
MnO	0.47	–	–	–	–	–	0.51	0.15	0.11	–	0.08	0.08	0.21	–	–	2.09	–	–	–	–	0.08
Na ₂ O	0.15	–	–	–	–	–	0.08	0.43	3.25	–	0.44	0.26	0.42	–	–	0.38	–	–	–	1.39	0.10
P ₂ O ₅	0.14	–	–	–	–	–	0.21	0.63	0.25	–	0.06	0.59	–	–	–	0.95	–	–	–	–	0.25
S	1.18	0.93	0.46	0.69	0.50	0.15	1.89	0.89	1.06	1.17	–	6.51	0.35	–	–	0.98	1.50	1.20	1.45	0.31	0.20
Si	–	17.00	14.00	15.43	15.37	–	–	12.15	–	23.01	–	–	0.00	–	13.80	–	–	–	8.50	20.28	–
SiO ₂	33.09	–	32.60	29.47	32.00	29.60	26.66	27.02	40.04	–	45.41	14.68	46.68	33.75	–	59.27	30.00	31.05	26.04	28.82	31.07
TiO ₂	–	–	–	–	–	–	0.28	0.37	0.54	–	0.22	0.25	0.61	–	–	0.73	–	–	0.10	–	0.49
Trace elements																					
Ag	0.00	–	5.00	–	–	–	–	–	–	–	–	–	0.00	–	–	–	–	–	–	–	–
Al	–	2.50	1.45	2.72	2.56	–	–	–	–	1.26	–	–	–	–	2.75	–	–	–	–	4.90	–
As	0.01	–	0.02	0.07	–	0.19	–	–	–	–	–	2.41	0.05	–	0.19	0.10	–	–	–	–	–
Bi	–	–	–	–	–	–	–	–	–	–	–	0.01	–	–	–	–	–	–	–	–	0.08
Ca	–	1.10	0.05	4.13	6.26	–	–	2.09	–	1.49	–	–	–	–	5.21	–	–	–	–	4.10	–
Cd	–	–	–	–	–	–	–	–	–	–	–	0.14	–	–	–	–	–	–	0.00	–	–
Co	–	0.20	0.02	1.51	1.21	0.05	–	0.12	–	–	–	0.02	0.07	–	–	0.02	1.00	–	0.31	–	1.20
Cu	0.67	0.67	1.05	1.48	0.82	0.99	0.65	1.14	1.09	1.53	1.45	2.75	0.87	0.97	1.02	1.85	0.50	1.25	1.51	1.40	1.43
Mg	–	1.70	0.56	2.15	2.53	–	–	0.97	–	0.18	–	–	–	–	0.78	–	–	–	–	2.00	–
Mn	–	–	0.02	0.14	–	–	–	0.34	–	–	–	–	–	–	–	0.12	–	–	–	0.46	–
Mo	0.00	–	0.26	0.01	–	–	–	–	–	–	–	–	0.04	–	–	0.01	–	–	–	–	0.02
Ni	0.00	0.69	0.00	0.18	–	0.05	–	0.06	–	–	–	0.01	0.04	–	–	0.01	2.00	–	0.04	0.00	0.03
Pb	0.27	–	0.03	0.56	0.9*	0.60	0.53	0.09*	–	–	0.05*	10.39	1.00	–	0.10	0.15	–	0.16	0.09	0.08	0.03
Sb	–	–	0.03	–	–	0.06	0.14	–	–	–	–	0.22	–	–	–	0.04	–	–	–	–	–
Ti	–	–	0.37	0.19	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Zn	4.34	–	0.84	1.32	6.95	2.79	1.27	0.61	0.84*	5.00	0.10	2.82	0.82	–	0.80	0.66	–	1.6*	0.75	1.40	0.08

* Reported in oxide form.

Table 2

Average chemical composition of copper smelter slag for major elements from over 80 studies globally.

Component	SiO ₂	FeO	Fe ₂ O ₃	CaO	Al ₂ O ₃	MgO	K ₂ O	S	MnO	TiO ₂	P ₂ O ₅	Na ₂ O
Content (wt.%)	33.18	32.15	31.93	6.21	5.88	2.02	1.53	1.19	0.42	0.40	0.39	0.06

Table 3

Average chemical composition of copper smelter slag for minor elements from over 80 studies globally.

Component	Ca	Al	Zn	Ag	Mg	Cu	Pb	Co	As	Ti	Ni	Mn	Sb	Mo
Content (wt.%)	3.05	2.59	1.83	1.67	1.36	1.19	0.94	0.48	0.38	0.28	0.24	0.22	0.10	0.06

roofing granules.

The copper slag is highly heterogeneous and chemically diverse. Thus, characterisation of the copper slag is fundamentally important in determining the best approach for metal recovery, assessment of environmental impacts, and its utilisation as a construction material. Knowledge of the characterisation of copper slag, physical and mechanical properties, the breadth of technology for metal recovery, and utilisation has enhanced considerably since publication of what is now regarded to be the landmark paper on copper slag by [Gorai et al. \(2003\)](#). [Piatak et al. \(2014\)](#) provided an extensive review on the characterisation of ferrous and non-ferrous slags and their environmental impacts as well as their role as a valuable resource for reuse and recycling. Engaging with these mainstream ideas, another in-depth review was put forward by [Potysz et al. \(2015\)](#) on the current knowledge about metallurgical slags including the chemical and phase composition, metal recovery, environmental risk, and fate. However, a critical unpacking of these ideas and review of current knowledge is needed to yield strategies capable of unlocking the resource potential of copper slag. In our reviews, we provide a more comprehensive study of copper slag waste as a potential world resource for a circular economy. Part I of our review, presented an overview of copper slag as a potential resource for cobalt and copper metals including figures on the global mine production, demand, and reserves of these metals. In this review (Part II), an overview of the chemical and mineralogical characterisation of copper slag are discussed. The average chemical composition of copper smelter slag from major producing countries is presented in [Table 1](#). The various processing strategies for metal recovery such as flotation, pyrometallurgy, hydrometallurgy and pyro-hydrometallurgy are discussed. The environmental impacts of copper slag have also been assessed. Finally, we present the utilisation of copper slag waste in construction as an example of environmental sustainability.

2. Characterisation of the copper slag

2.1. Chemistry of copper slag

The chemical composition of slag is mainly focused on major, minor and trace elements, loss on ignition, C and S species, and stable isotopes. The commonly used techniques for sample analysis are X-Ray Fluorescence (XRF), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Atomic Absorption Spectroscopy (AAS), and automated Elemental Analysis (EA) by combustion for C, N, S, and H. Other methods used include Infrared Analysis (IR) for C and S, Neutron Activation (NA), Hydride Generation (HG) for Hg, and Gravimetric and Volumetric Analysis and Photometry (GVP) ([Piatak et al., 2014](#)). The combination of these analytical tools can produce a detailed chemical composition of copper slag. These methods have also been applied in research involving laboratory simulations of weathering and alterations of the slag materials ([Parsons et al., 2001](#); [Ettler et al., 2009](#); [Kierczak and Pietranik, 2011](#); [Piatak et al., 2014](#)).

The bulk chemical composition of copper slags may vary depending

on the pyrometallurgical technique used; the phase composition of the copper slag can be quite diverse ([Gbor et al., 2000](#); [Gorai et al., 2003](#); [Lottermoser, 2006, 2010](#); [Potysz et al., 2015](#)). For example, studies on air cooled and quenched copper slag revealed that the diversity of phases is largely influenced by the cooling rates. [Ravindra et al. \(2017\)](#) identified fayalite as the principal mineral in most of the copper slag samples with contents of up to 57% in air-cooled slags and 15% in quenched copper slag samples. In another study, [Potysz et al. \(2015\)](#) noted that phase diversity was less in quenched slags than in slowly cooled slags. This could be because crystallisation does not occur in quenched slags due to rapid cooling. Crystallisation of phases was found to occur closer to equilibrium during slow cooling which led to formation of several phases ([Kierczak and Pietranik, 2011](#)). These findings were consistent with the observation that rapid cooling leads to the formation of amorphous phases and segregation of metal oxides while vitreous and crystalline components are formed during slow cooling ([Gorai et al., 2003](#); [Piatak et al., 2004](#); [Kuo et al., 2008](#); [Potysz et al., 2015](#); [Ravindra et al., 2017](#)). This shows that the cooling rate of the slag has a significant influence on the phase composition. Hence the bulk chemistry of the slag can be an important consideration in selecting the processing method of copper slag. [Table 1](#) shows a summary of the average chemical composition of copper smelter slags obtained from over 80 studies covering 21 countries. The average chemical composition of copper slag was calculated by considering studies in each country from different copper smelting sites. The detailed chemical composition of copper slag from different parts of the world is presented in [Table 4a](#) and [Table 4b](#) in Appendix A at the end of the article.

[Anand et al., 1980](#); [Tümen and Bailey, 1990](#); [Yucel et al., 1992](#); [Jones et al., 1996](#); [Mobasher et al., 1996](#); [Acma et al., 1997](#); [Herreros et al., 1998](#); [Kiyak et al., 1999](#); [Marghussian & Maghsoodipoor, 1999](#); [Imris et al., 2000](#); [Agrawal et al., 2000](#); [Arslan & Arslan, 2002](#); [Lottermoser, 2002](#); [Banza et al., 2002](#); [Manasse & Mellini, 2002](#); [Banda et al., 2002](#); [Sáez et al., 2003](#); [Gbor et al., 2003](#); [Jalkanen et al., 2003](#); [Piatak et al., 2004](#); [Gonzalez et al., 2005](#); [Gbor et al., 2006](#); [Bulut, 2006](#); [Lottermoser, 2006](#); [Maldonado, 2006](#); [Carranza et al., 2009](#); [Busolic et al., 2009](#); [Ettler et al., 2009](#); [Das et al., 2010](#); [Khanzadi and Behnood, 2009](#); [Chew and Bharati, 2009](#); [Tshiongo et al., 2010](#); [Yang et al., 2010](#); [Kierczak and Pietranik, 2011](#); [Vítková et al., 2010, 2011](#); [Muravyov et al., 2012](#); [Huanosta-Guitierrez et al., 2012](#); [Kim et al., 2013](#); [Nadirov et al., 2013, 2017](#); [Wang et al., 2013](#); [Urosevic et al., 2015](#); [Heo et al., 2016](#); [Fan et al., 2017](#); [Subrata et al., 2015](#); [Shamsi et al., 2015](#); [Addis et al., 2016](#); [Ambily et al., 2015](#); [Roy et al., 2015](#); [Dimitrijevic et al., 2016](#); [Kakengela et al., 2016](#); [Potysz et al., 2016](#); [Prasad and Ramana, 2016](#); [Kaksonen et al., 2016](#); [Sarfo et al., 2017](#); [Kaksonen et al., 2017](#); [Sharma and Khan, 2017](#); [Potysz and Kierczak, 2017](#); [Meshram et al., 2017](#); [Yuksel et al., 2017](#); [Turan et al., 2017](#); [Guo et al., 2018](#); [Potysz et al., 2018](#); [Nadirov and Mussapyrova, 2019](#); [Gupta and Siddique, 2020](#).

The copper smelter slags are highly heterogeneous and chemically diverse ([Table 2](#)). The bulk chemical composition of copper slags mainly depends on the metallurgical processes from which they are derived, which are determined by type of concentrate, type of fluxes, type of furnaces and cooling rates ([Gbor et al., 2000, 2003](#); [Gorai et al., 2003](#); [Alter, 2005](#); [Lottermoser, 2010](#); [Piatak et al., 2014](#); [Potysz et al., 2015](#)).

The principal slag constituents are the following oxides: silica (SiO_2), ferrous oxide (FeO), ferric oxide (Fe_2O_3), limestone (CaO) and alumina (Al_2O_3). Fayalite (Fe_2SiO_4) is often expressed as $(2\text{FeO})\cdot\text{SiO}_2$ to emphasise its constitution of two moles of FeO for every SiO_2 ; similarly magnetite Fe_3O_4 can be expressed as $\text{FeO}\cdot\text{Fe}_2\text{O}_3$. Indeed the oxides display average bulk chemical compositions of 33.18 wt% SiO_2 , 32.15 wt% FeO , 31.93 wt% Fe_2O_3 , 6.21 wt% CaO and 5.88 wt% Al_2O_3 with lesser amounts (between 0.06 and 2.02 wt%) for MgO , K_2O , S , MnO , TiO_2 , P_2O_5 , and Na_2O (Table 2).

The studies also show high concentrations of metals and metalloids with averages of 3.05 wt% Ca , 2.59 wt% Al , 1.83 wt% Zn , 1.67 wt% Ag , 1.36 wt% Mg , 1.19 wt% Cu , 0.94 wt% Pb , and 0.48 wt% Co (Table 3). Other metals and metalloids such as As , Ti , Ni , Mn , Sb , and Mo were also detected but in much lesser amounts (lower than 0.4 wt%).

The grade of Co and Cu in the slag is higher than the average ore grade for most mines due to depletion of high-grade deposits. These minor elements are present in the slag as entrained sulphides, oxides and metallic elements. The older copper slags are observed to contain higher amounts of metals because older technologies were not as effective as modern ones (Lottermoser, 2002; Potysz et al., 2015).

2.2. Mineralogy of copper slag

The mineralogical composition is fundamentally important in determining the best approach for metal recovery from the copper slag. The mineralogical characterisation of copper slags has commonly been performed using Scanning Electron Microscopy (SEM), X-ray powder diffraction (XRD), X-ray fluorescence spectroscopy (XRF), Electron Microprobe Analysis (EMPA), and Raman spectroscopy.

Several studies on different types of copper slags have been able to identify the most frequently occurring mineral phases. Generally, copper slags constitute fayalite and silicate glassy matrices as major components with other phases such as crystalline oxides, sulphides, metallic elements, alloys, and intermetallic compounds as minor constituents (Gorai, et al., 2003; Bulut, 2006; Ettler et al., 2009; Piatak et al., 2014; Potysz et al., 2015; Dimitrijevic et al., 2016; Kaksonen et al., 2016; Meshram et al., 2017; Ravindra et al., 2017). In other studies, (Altudogan and Tumen, 1997) and Deng and Ling (2007) found that copper converter slag consisted principally of fayalite and magnetite as the host minerals. Other studies found some common silicates with compositions corresponding to Melilite ($(\text{Ca}, \text{Na})_2(\text{Al}, \text{Mg}, \text{Fe}^{2+})(\text{Si}, \text{Al})_2\text{O}_7$) and willemite (Zn_2SiO_4) (Lottermoser, 2002; Manasse and Mellini, 2002; Ettler et al., 2003). Granulated slags have been observed where most of the calcium and chloride and the iron were present as magnetite, fayalite and ferrosilite (Meshram et al., 2017). The fayalite structure in copper slags is produced when pyrite is oxidised to iron oxide in the presence of silica and sometimes contains minor amorphous silica phases (Li et al., 2008).

Shen and Forssberg (2003) observed that different copper slags have different forms of copper minerals such as oxides or sulphides or a mixture of both. This observation was consistent with Potysz et al. (2015) who observed that copper slags were composed of various synthetic analogues of naturally occurring mineral phases. The sulphide minerals are mostly associated with metallic elements and the common ones found in copper slags include bornite (Cu_5FeS_4), chalcocite (Cu_2S), and chalcocite (Cu_2S) (Parsons et al., 2001; Lottermoser, 2002; S  ez et al., 2003; Ettler et al., 2009;   lvarez-Valero et al., 2009; V  tkov   et al., 2010; Kierczak et al., 2013; Nadirov et al., 2013; Potysz et al., 2015; Dimitrijevic et al., 2016; Kaksonen et al., 2016; Sarfo et al., 2017). The other sulphide phases present within the copper slags are pyrite (FeS_2), galena (PbS), sphalerite ($(\text{Zn}, \text{Fe})\text{S}$), pyrrhotite ($\text{Fe}(1-\text{X})\text{S}$) and wurtzite ($(\text{Zn}, \text{Fe})\text{S}$) whereas covellite (CuS), cubanite (CuFe_2S_3), digenite (Cu_9S_5), troilite (FeS), and pentlandite ($(\text{Fe}, \text{Ni})_9\text{S}_8$) are rarely observed (Lottermoser, 2002; Ettler et al., 2009;   lvarez-Valero et al., 2009; Piatak et al., 2014).

The principal iron oxide minerals found in copper slags include

fayalite (Fe_2SiO_4), spinels (MgAl_2O_4), hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO) (Parsons et al., 2001; Manasse et al., 2001; Lottermoser, 2002, 2010; S  ez et al., 2003; Piatak et al., 2004; Bulut, 2006; Ettler et al., 2009; V  tkov   et al., 2010; Mateus et al., 2011; Ravindra et al., 2017). A minor amount of oxides has also been identified in copper slags, such as leucite ($\text{K}(\text{AlSi}_2\text{O}_6)$), hercynite (FeAl_2O_4) (Bulut, 2006; Kierczak and Pietranik, 2011; Potysz et al., 2016). Pyroxene group minerals such as diopside ($\text{FeCaSi}_2\text{O}_6$) and hedenbergite ($\text{CaFeSi}_2\text{O}_6$) and the olivine group minerals kirschsteinite ($\text{CaFe}^{2+}\text{SiO}_4$) and forsterite (Mg_2SiO_4) are also found in copper slags (Lottermoser, 2002; Manasse and Mellini, 2002; S  ez et al., 2003; Piatak et al., 2004; V  tkov   et al., 2010; Ravindra et al., 2017). Chrysocolla ($(\text{CuAl})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \times n(\text{H}_2\text{O})$), leucite (KAlSi_2O_6), wollastonite (CaSiO_3), pyroxomangite (MnSiO_3), iscorite ($\text{Fe}^{2+}5\text{Fe}^{3+}2\text{SiO}_{10}$) and titanite (CaTiSiO_5) are also occasionally found (Lottermoser, 2002; Manasse and Mellini, 2002; S  ez et al., 2003).

3. Overview of the copper slag processing strategies

There are various techniques for recovering metals from the copper slags with attention given to flotation, hydrometallurgy, pyrometallurgy and an integration of pyrometallurgy and hydrometallurgy (pyro-hydrometallurgy).

3.1. Flotation for processing of copper slag

Froth flotation is the most common method that utilises the difference in surface properties between the minerals to separate the valuable minerals from the unwanted gangue minerals. The enriched product derived from the process is called the Concentrate, and the gangue or unwanted material is known as Tailings. A third product that consists of valuable and gangue minerals still locked together is called Middlings. Such a fraction is usually re-ground to further liberate the particles.

The flotation approach is the only beneficiation method considered in this study because it has been found to be an important alternative in the recovery of copper from secondary sources such as copper slag. The flotation has been investigated for recovery of metals from copper slag using collectors, frothers, modifiers and depressants. The main parameters considered for the flotation approach are particle size, collector dosage and pH. Copper slag flotation is similar to sulphide ore flotation (Osborn et al., 1990; Arslan and Arslan, 2002; Gulay, 2006). The copper slag is fed into the flotation unit and the sulphide minerals (Cu_2S , Cu_5FeS_4) are floated with the help of collector and frother reagents to produce a concentrate.

The flotation method has mainly been investigated on the two types of slags namely, reverberatory and smelter slags. The reverberatory slag is produced from the reverberatory smelting furnace and usually produces the slag that is more dilute in copper of about 0.6% and is discarded without slag recovery treatment (Davenport et al., 2002). The smelter slag is produced from the smelting furnaces and contains copper with average of 1.2%. The term 'smelter slag' is being addressed in a more general term without any specific emphasis on the type of furnaces such as Flash, Noranda, Mitsubishi, Reverberatory smelting furnaces. Sarrafi et al. (2004) investigated the recovery of copper from reverberatory furnace slag utilising flotation. The parameters such as cooling rate, particle size, collector dosage, pH and flotation time were studied. The results show that for an air-cooled slag at optimal conditions, a copper recovery of 72% was achieved in one stage flotation with a copper concentrate grade of 12.6% using R407 collector at a dosage of 30 g/t. Further, Sarrafi et al. (2004) found that the copper recovery was affected by the cooling rate of molten slag which increased to 84% when the slag was cooled slowly. In a similar study, Das et al. (2010) explored the recovery of copper values from an Indian smelter slag by applying flotation technique using conventional sodium isopropyl xanthate (SIPX) as the collector. The effects of flotation parameters such as pH and collector concentration were investigated. The findings under

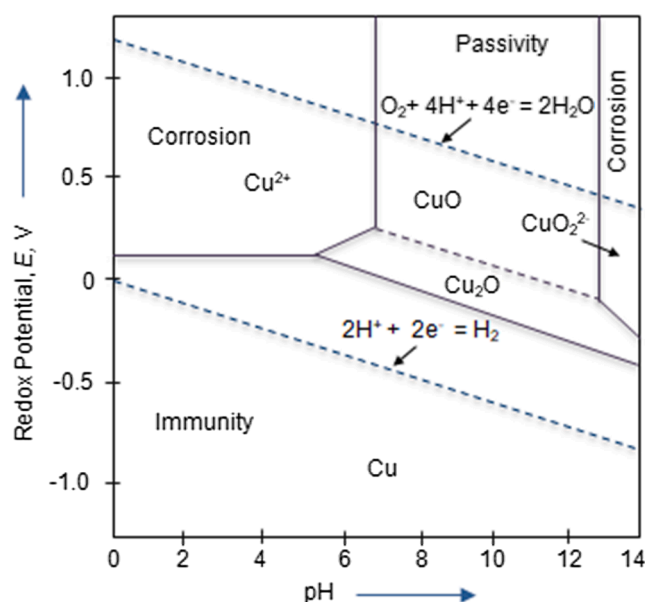


Fig. 1. Pourbaix diagram for copper in dilute aqueous solution at normal temperature (Lossin et al., 2001).

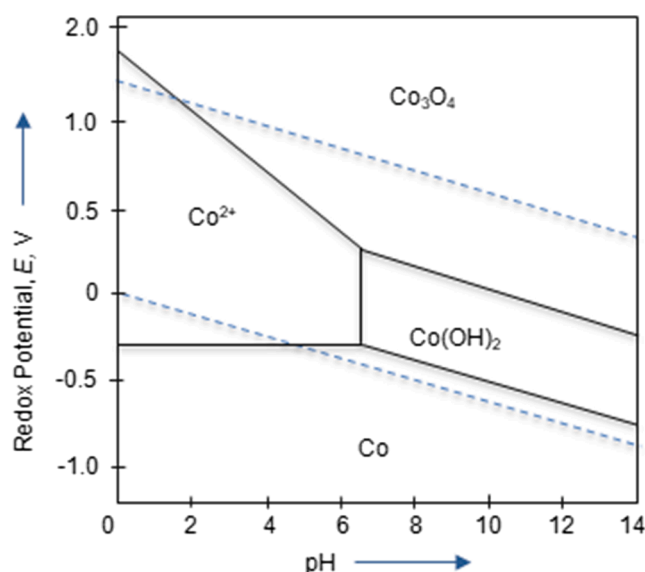


Fig. 2. Pourbaix diagram for cobalt in dilute aqueous solution at normal temperature (Ghazitabar et al., 2018).

optimum flotation conditions show copper grade of about 21% with the copper recovery of more than 80%. The effect of grinding time on flotation recovery of copper smelter slags within the Bardaskan district, Iran was investigated (Shamsi et al., 2015). The results obtained for the flotation tests at optimal conditions showed a copper recovery of 79.89% after grinding the material for 85 min to a particle size of 80% passing 48 μm . Kim et al. (2013) studied a physico-chemical separation process for upgrading iron from waste copper slag. The process involved the crushing of the waste copper slag between 150 and 203 μm followed by the reduction reaction at 1250 $^{\circ}\text{C}$ for 1.5 h and dry magnetic separation. They found that a magnetic product containing over 65 wt% of Fe was obtained using the magnetic separation under a magnetic field strength of 0.03 T at percentage iron recovery of 85%.

The recovery of copper from smelter slag using flotation approach was studied (Fan et al., 2017). Three key factors affecting the flotation process such as grinding fineness, collector dosage, and pH were

investigated. The results obtained were a copper concentrate grade of 14.47% and a copper recovery of 79.66%, at a grinding fineness of 80% smaller than -0.074 mm , with reagent dosage of 50 g/t for butyl xanthate, and a pH value of 10. In a similar study, the flotation of copper sulphide from copper smelter slag using multiple collectors involving sodium iso-propyl xanthate (SIPX), sodium di-ethyl dithiophosphate (DTP), and alkyl hydroxamate at various dosages was investigated (Roy et al., 2015). The findings show that a higher copper recovery of 84.82% was obtained using a 40:160 g/t mixture of sodium iso-propyl xanthate with di-ethyl dithiophosphate compared to a copper recovery of 78.11% when using the best single collector. Similarly, a high copper recovery of 83.07% was also achieved using a 160:40 g/t mixture of sodium iso-propyl xanthate with alkyl hydroxamate.

However, studies have shown that most of the copper and cobalt in the slag are in the oxide phase which cannot be treated directly by the flotation method (Dimitrijevic et al., 2016). Similar observations were made by Hara and Jha (2016) that the majority of copper in the slag is in the oxide phase and nearly all the cobalt is chemically combined with silica, iron, calcium and aluminium oxides, making separation via flotation extremely difficult. A study on surface modification of oxide minerals with ethanediamine (Feng et al., 2018) revealed that oxide minerals are more difficult to float because they exhibit a higher solubility and extensive hydration compared to sulphide minerals. Holland et al. (2019) suggest that the processing and cooling rates of the copper slag after smelting are important considerations prior to milling and flotation operations for efficient metal recovery. In principle, only metallic copper and sulphide minerals can be extracted efficiently using flotation (Deng and Ling, 2007; Meshram et al., 2017).

3.2. Hydrometallurgical approach for processing of copper slag

The treatment of non-ferrous minerals is often achieved via a hydrometallurgical approach for economic reasons and relatively lower environmental impacts. The hydrometallurgical route by leaching is the most common method used in low grade metal recovery processes. This has been investigated for the extraction of metals from copper slag using different values of parameters such as leaching system, concentration of an extractant, temperature, solid/liquid ratio and leaching time. The focus has been on atmospheric leaching using lixiviants such as acids, bases and salts. Many of these lixiviants form aqueous solutions are capable of dissolving metals from ores or concentrates and slags. There are several criteria an aqueous lixiviant should satisfy, with reagent cost being one of the more important. Other criteria are the ability to selectively dissolve the desired metal, the ease of procuring and handling, the ability to regenerate and reuse reagents, and the extent to which it corrodes process equipment.

Pourbaix (or Eh-pH) diagrams are an effective tool used in designing leaching processes as they give an indication of the dissolution behaviour of metals and the feasibility of electrochemical reactions. The figure below shows an example of a Pourbaix diagram for the Cu – H₂O system which indicates four regions of different behavior; i.e. under oxidising conditions a region of corrosion is shown in acidic environments, followed by passivity in alkaline solutions, second corrosion region is indicated in very highly alkaline solutions, while under reducing conditions a wide region of immunity is indicated at any pH shown in the diagram (Fig. 1).

The corrosion region gives the standard electron potential in which the copper metal is stable (Lossin et al., 2001). In this region the dissolution of copper is possible in non-oxidising acids like dilute sulphuric and hydrochloric acid as well as oxidising acids such as hot concentrated sulphuric acid and nitric acid. Additionally, copper can be leached in ammonia solutions in the presence of oxygen forming stable complexes. Redox systems such as copper(II) or iron(III) chloride solutions dissolve the copper in the corrosion region. In the passivity region, electrochemical reactions are impossible due to kinetic phenomena and, in the immunity region, the electrochemical reactions are

thermodynamically not feasible (Lossin et al., 2001). The behaviours of copper and cobalt in a water system show similar trends. The figure below shows the Pourbaix diagram for cobalt in a dilute aqueous solution at room temperature.

The Pourbaix diagram (Fig. 2) shows that the cationic form of cobalt (Co^{2+}) dominates at pH values lower than 6. The cobalt is stable and the presence of oxygen-containing groups in the solution creates conditions for electrostatic attraction between the positively charged and negatively charged groups (Ghazitabar et al., 2018). This electrostatic attraction leads to the formation of cobalt hydroxides and/or cobalt oxides which can be leached effectively.

A number of experiments have investigated the treatment of copper slag using sulphuric acid (Anand et al., 1983; Baghalha et al., 2007) or combining sulphuric acid with another extractant such as ammonium sulphate (Sukla et al., 1986), sodium chlorate (Yang et al., 2010) or potassium dichromate (Altundoğan et al., 2004; Boyrazli et al., 2006; Nadirov and Mussapyrova, 2019). Leaching with sulphuric acid using oxidants such as hydrogen peroxide (Basir and Rabah, 1999; Banza et al., 2002) has also been proposed. A method of combining two strong acids (sulphuric acid and nitric acid) has been studied by Tshiongo et al. (2010) as well as combining organic acid (citric acid) and inorganic (sulphuric acid) (Meshram et al., 2017). Several studies have investigated the leaching of copper slag using bases and salts such as ferric chloride (Anand et al., 1980), ferric sulphate (Altundoğan and Tümen, 1997; Bulut, 2006; Bese, 2007; Carranza et al., 2009), ammonium sulphate (Sukla et al., 1986), ammonium chloride (Nadirov et al., 2013; Borisov et al., 2011), chlorine solution (Herreros et al., 1998; Bese et al., 2003) and ammonium hydroxide (Nadirov et al., 2017; Aracena et al., 2019). Hydrochloric acid with ammonium hydroxide has also been investigated (Basir and Rabah, 1999). High temperature leaching to improve the extraction efficiency has also been conducted (Basir and Rabah, 1999; Arslan and Arslan, 2002; Deng and Ling, 2007; Bese, 2007; Carranza et al., 2009; Nadirov et al., 2013).

3.2.1. Leaching with acids

Sulphuric acid (H_2SO_4) is the most widely used lixiviant because of its low price, assertiveness, and general accessibility. It is considered to be an efficient lixiviant for the leaching of metal oxides and one of the strong acids that is soluble in water at all concentrations. It can be used in dilute or concentrated form or combined with oxygen. Sulphuric acid has the potential for local utilisation because it is a major by-product of copper smelters that could be used onsite to leach copper slags. Several studies performed using sulphuric acid as the leaching agent for copper slags have shown high metal extraction efficiencies (Anand et al., 1983; Sukla et al., 1986; Basir and Rabah, 1999; Banza et al., 2002; Arslan and Arslan, 2002; Altundoğan et al., 2004; Bese, 2007; Baghalha et al., 2007; Deng and Ling, 2007; Yang et al., 2010). The recovery of metal values from the copper slag using sulphuric acid by Yang et al. (2010) significantly improved the extraction of metals, giving 98%, 97% and 89% for cobalt, zinc and copper respectively. The process also provided faster filtration and significantly reduced the adverse effects of silica and iron (III) oxides on the recycling of target value metals. However, further investigations are needed to reduce the excessive acid and lime consumption in this process.

Oxidative high-pressure acid leaching with autoclaves has been investigated (Baghalha et al., 2007). The results show a metal extraction of 80% in the presence of oxygen, whereas in the absence of oxygen extractions of only 0%, 37% and 20% for Cu, Co and Ni respectively were achieved. Leaching with sulphuric acid at elevated pressure has been carried out (Anand et al., 1983) with an improvement in the leaching extraction and solid-liquid separation. Further studies involving high pressure oxidative acid leaching have been conducted (Li et al., 2008). Bese (2007) investigated the effect of ultrasonic energy on the dissolution of copper from copper converter slag. The effects of parameters such as temperature, acid concentration, ferric sulphate concentration and time were also studied. The findings indicate the

extraction efficiencies of copper, zinc, cobalt and iron of 89.28%, 51.32%, 69.87% and 13.73% respectively whereas in the absence of ultrasound, the efficiencies were lower, 80.41%, 48.28%, 64.52%, and 12.16%, respectively (Bese, 2007).

Citric acid is a r-hydroxyl tricarboxylic acid and is well known for its chemical versatility in leaching transition metal ions. Citric acid leaching of base metals (copper, cobalt, nickel and iron) from copper granulated slag was studied (Meshram et al., 2017). The method involved the leaching of the copper slag using citric acid to recover cobalt, nickel and iron followed by leaching of the residue containing a high copper concentration with sulphuric acid. The study showed that a maximum recovery of 4.47% of Cu, 88.3% Co, 95% Ni and 93.8% Fe was obtained in the first stage of leaching using citric acid at room temperature at 10% pulp density, and 66–72% of the copper was recovered from the leach residue in the second stage.

Nitric acid (HNO_3) is a powerful oxidising reagent and reacts violently with many metallic compounds in leaching. Tshiongo et al. (2010) investigated the use of nitric acid with ammonia solution as leaching agents for copper slags with different cooling methods such as water quenching, air cooling and furnace cooling. They found that the cooling rate of the slag affected the leaching of base metals as it changed the phase distribution in the slag and the base metal distribution within the phases. Tshiongo et al. (2010) observed that fast cooling of the slag prevented crystallisation to take place and produced an amorphous phase which enclosed the base metals. However, they found that amorphous slags were more leachable in acid medium (HNO_3) achieving recovery of 46% of Cu, 95% Co, 85% Zn, 92% Pb and 79% Fe than in basic medium (NH_4OH).

Research using sulphuric acid as a lixiviant has shown a positive correlation between acid concentration and extraction efficiency for different leaching parameters (Anand et al., 1983; Basir and Rabah, 1999; Altundoğan et al., 2004; Yang et al., 2010; Deng and Ling, 2007; Baghalha et al., 2007; Potysz et al., 2016). Some studies noted that although there is high metal extraction efficiency of 93–100%, extraction from silica rich slag involves a high consumption of sulphuric acid and yields silica gel suspended in a solution with high concentrations of iron (Anand et al., 1983; Deng and Ling, 2007; Yang et al., 2010; Potysz et al., 2016; Hara and Jha, 2016). This is due to the fact that metals such as cobalt and copper are dissolved in the spinel oxide, ferrite and silicates. The high consumption of sulphuric acid and lime, as well as poor settling and filtration characteristics caused by the formation of iron hydroxide precipitates and silica gel, limits the usefulness of the process (Yang et al., 2010; Hara and Jha, 2016). To overcome these challenges, other studies have investigated combining acids with oxidants for recovery of metal values from copper slag.

3.2.2. Leaching with acids and oxidants

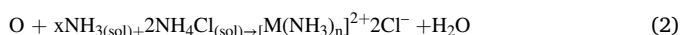
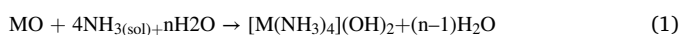
Oxidants are effective leaching agents for naturally occurring minerals that are susceptible to oxidation processes. Oxygen, hydrogen peroxide, sodium chlorate and Fe(II)/Fe(III) are lixiviants that are considered effective oxidants for leaching of copper slags (Anand et al., 1983; Basir and Rabah, 1999; Banza et al., 2002; Baghalha et al., 2007). The use of oxidants as leaching agents can be an efficient solution to overcoming the problem of silica gel formation and simultaneously remove iron from solution through the oxidation process. Banza et al. (2002) considered hydrogen peroxide (H_2O_2) as an oxidant for extraction of metals from copper slag while preventing the problem of silica gel formation. The study achieved extraction efficiencies of 80% of Cu, 90% Co, 90% Zn, and reduced Fe to 5%. A similar study by Yang et al. (2010) revealed that the use of oxidants such as sodium chlorate (NaClO_3) and calcium hydroxide (Ca(OH)_2) as a neutralising agent also reduced silica gel formation, and facilitated filtration of the solution. The results achieved metal recoveries of 89%, 98%, 97% for Cu, Co, and Zn respectively while the iron was as low as 0.02%. Sodium chlorate (NaClO_3) prevents the formation of silica gel due to the oxidation of Fe^{2+} to Fe^{3+} .

Anand et al. (1983) conducted research on the leaching of copper slag using high oxygen pressure and the results showed improved metal extraction efficiencies of 90% of Cu and 98% of Co. It was observed that oxygen availability was an important factor for the oxidation of Fe^{2+} which minimised the extraction of iron. For example, at lower oxygen pressure the extraction efficiency of Fe was 1.2% whereas at higher oxygen pressure it was 0.81% Fe. These findings were consistent with the study conducted by Basir and Rabah (1999) who found that oxygenated conditions can improve copper and cobalt extraction efficiencies while simultaneously achieving a low iron extraction.

The effects of sulphuric acid and potassium dichromate concentrations on the extraction of metals from copper slag have been investigated (Altundoğan et al., 2004; Boyrazli et al., 2006; Nadirov and Mussapyrova, 2019). Altundoğan et al. (2004) studied the leaching of copper converter slag using sulphuric acid (H_2SO_4) in the presence of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). The most suitable lixiviant composition was determined to be 0.25 M (H_2SO_4) and 0.1 M ($\text{K}_2\text{Cr}_2\text{O}_7$) with a solid/liquid ratio of 10 g/L, temperature of 25 °C and contact time of 120 min. The results indicate that the presence of $\text{K}_2\text{Cr}_2\text{O}_7$ gave an extraction efficiency of 81.15% of Cu while adversely affecting the extraction of other metals such as Co, Zn and Fe with efficiencies of 12.0%, and 10.27%, and 3.15% respectively. In a similar study, Boyrazli et al. (2006) studied the effects temperature (25 to 70 °C), leaching time (5 to 240 min) and solid/liquid ratio (5 to 400 g/L). The results indicated that the highest extraction efficiency of 99.6% of Cu was obtained at 0.25 M (H_2SO_4), 0.1 M ($\text{K}_2\text{Cr}_2\text{O}_7$), 70 °C and leaching for 120 min. However, the extraction efficiencies for Co, Zn and Fe were very low at 42.09%, 49.86% and 27.59% respectively. It was noted that the extraction of Co, Zn and Fe increased only when the leaching was conducted at elevated temperatures. This could have been due to the decrease in the adsorbed amounts of dichromate ions responsible for passivation effects. These findings were consistent with a more recent study on the H_2SO_4 - $\text{K}_2\text{Cr}_2\text{O}_7$ system for leaching of copper, zinc and iron from copper smelter slag (Nadirov and Mussapyrova, 2019). The results show that the presence of dichromate had a positive influence on copper recovery, giving an extraction efficiency of 68% of Cu. However, the recovery of zinc and iron decreased significantly to 4% and 5% respectively under the same conditions. They observed that the copper extraction efficiency increased with dichromate concentration. It was suggested that the decrease in the extraction of other metals could have been due to the precipitation and surface passivation effects caused by dichromate ions (Nadirov and Mussapyrova, 2019).

3.2.3. Leaching with bases and salts

A number of studies have shown that using these agents has several advantages and can eliminate problems associated with leaching using common acids (Potysz et al., 2015; Nadirov et al., 2017; Aracena et al., 2019). For example, ammonium hydroxide (NH_4OH), which is also known as aqua ammonia in aqueous solutions, can dissolve various metal oxides and hydroxides such as copper (II) hydroxide to form ammine complexes. Ammonium chloride is a safe non-volatile agent and an environmentally friendly crystalline substance at room temperature. The physico-chemical principles for metal recovery using ammonia and ammonium are based on the behaviour of the H_2O - NH_3 - NH_4Cl system containing metal amines, and the phase equilibria for liquid and solid, and liquid and vapour (Nadirov et al., 2017). The following equations show the dissolution of metals in an aqueous solution of NH_4OH .



where M = metals e.g. Cu; $n = x + 2$.

Equation (1) shows the dissolution of metals in the absence of Cl^- ions and Equation (2) in the presence of Cl^- ions.

Anand et al. (1980) investigated the leaching of copper slag using ferric chloride and observed that the extraction of copper increased with

an increase in ferric ions. The study revealed that the extractant was most efficient for leaching of copper minerals giving an extraction of 92% of the copper. However, low recoveries were obtained for nickel (23%) and cobalt (24%). Reduction roasting improved the nickel and cobalt extraction efficiencies to 95% and 80% respectively but the copper efficiency was reduced to 82%. Bese et al. (2003) considered the treatment of converter slag using chlorine saturated water. The optimum conditions for copper dissolution, while maintaining the level of iron dissolution were determined and a copper extraction efficiency of 98.35% was obtained. In a similar study, Herreros et al. (1998) performed the leaching of copper reverberatory slag using chlorine solution. They analysed the effects of stirring speed, particle size, initial chlorine and chloride concentrations, and temperature. Most of the copper was in the form of metallic copper, chalcocite, bornite and other complex sulphides, and mineral phases were liberated at particle sizes less than 20 μm . Copper extraction reached a maximum of 80% with iron solubilisation at a low level of about 5%.

Borisov et al. (2011) observed that the reaction of oxides and sulphides of some metal-bearing compounds such as CaO, ZnO, CuS, FeS, ZnS, and Fe_2O_3 leads to formation of chloro-metallate complexes such as $(\text{NH}_4)_2\text{ZnCl}_4$ and $(\text{NH}_4)_4\text{CuCl}_3$. These complexes can be further decomposed into chlorides. The results revealed that oxides of silicon and aluminium do not react with ammonium chloride which makes it a good leaching agent for silicate materials. Ammonia solutions containing ammonium chloride were found to be effective for the extraction of Zn and Cu from copper smelter slag (Nadirov et al., 2017). The study used the central composite rotatable design and approximation method to determine the optimum conditions for recovery of copper and zinc. The model successfully predicted the responses, and maximum copper and zinc recoveries of 81.16% and 56.48%, respectively were obtained. In a recent study by Aracena et al. (2019), a higher copper recovery of 87.7% has been reported using an ammonia column system for leaching of copper converter slag.

3.3. Pyrometallurgical approach for processing of copper slag

Pyrometallurgy involves chemical reactions of solids, gases or molten materials at elevated temperatures in a furnace. The technique includes processes such as calcination, smelting, converting and fire refining. Pyrometallurgical extraction of metals such as nickel, cobalt and copper from copper slag using a carbonaceous reducing agent in a DC arc furnace has been demonstrated (Jones et al., 1996). To show that metal extraction from copper slag can be enhanced using pyrometallurgical processes, a pilot plant was developed at Mintek, South Africa, and the process was then implemented on an industrial scale for recovery of cobalt from copper slag in a DC arc furnace at the Chambishi smelter, Zambia. Using power levels of about 1–2 MW, approximately 840 tons of dump slag was processed with good cobalt extraction and 100 tons of cobalt-bearing alloys were produced. However, the plant closed down as it could not run economically and efficiently due to the high energy requirements of the DC arc furnace (Mututubanya, 2013).

The carbothermal reduction of copper slags at temperatures of 1400–1800 °C in a submerged type DC arc furnace was investigated by Acma (1997). The study demonstrated that copper slag can be carbothermally smelted with partial reduction of iron oxide (FeO) to a metallic phase comprising of copper and other metals. Thereafter, the material was leached with H_2SO_4 and the solution purified with H_2S to separate CuS. Fe was precipitated as goethite. It was observed by Acma (1997) that the faulted structure with sulphur content over 2.9% favoured cobalt dissolution giving a high cobalt recovery of 99%. Banda et al. (2002) investigated carbothermic reduction of copper smelter slag under the influence of slag modifiers. In this study the use of rutile (TiO_2) as a slag modifier was found to produce a more selective recovery of cobalt compared to fluorspar (CaF_2) and lime (CaO) modifiers. However, TiO_2 was found to produce lower overall recoveries for cobalt at various levels of addition compared to the other modifiers. The ratio

of cobalt to iron recovery increased when rutile was added which was not the case with the other two modifiers. Yuçel et al. (1992) studied the treatment of ancient Kure copper slag by a carbothermal reduction process in a DC arc furnace at temperatures between 1430 °C and 1480 °C with maximum cobalt recovery of 95.7% and copper recovery of 90% achieved in a closed system. Another method was developed by Hara and Jha (2016) for direct reduction and sulphurisation of copper slag with activated charcoal, giving the highest copper recovery of 90% at 1323 K. The authors observed that although the plasma-based smelting is quite energy efficient with flexible control of the temperature of the melted material, the main disadvantage is that it requires energy in subsequent steps.

3.4. Pyro-hydrometallurgical approach for processing copper slag

As earlier mentioned, the roasting of copper slag followed by water or acid leaching is the most common method used in pyro-hydrometallurgical processing of copper slag. In experiments, the effects of roasting time, acid/slag ratio, roasting temperature and the application of thermal decomposition prior to leaching on metal dissolution have been investigated. The roasting of copper sulphide produces a calcine which is later processed using the hydrometallurgical route. Extensive research has been carried out on the roasting of copper slag using roasting agents such as sulphuric acid (H_2SO_4) (Anand et al., 1981; Sukla et al., 1986; Arslan and Arslan, 2002; Dimitrijevic et al., 2016; Deng and Ling, 2007), pyrite (FeS_2) (Tümen and Bailey, 1990), ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) (Altundogan and Tümen, 1997), graphite (Bulut, 2006) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) (Sukla et al., 1986) to yield metal sulphates.

Tümen and Bailey (1990) investigated the sulphation roasting of primary and secondary slags using pyrite followed by hot water leaching of the calcines. It was observed that the addition of pyrite increased the recovery of copper with an extraction efficiency of 95% from the primary converter slag and iron contamination of around 2%. However, using this process Co, Ni and Zn could not be efficiently extracted from the converter slag with only 58%, 35% and 29%, efficiencies respectively. Solid state carbothermic reduction in an inert nitrogen atmosphere was carried out using charcoal as a reducing agent in the temperature range of 600 °C to 1000 °C followed by sulphuric acid leaching (Mututubanya, 2013). The process involved reduction of the oxides of Co, Ni and Cu, while retaining the maximum possible quantity of Fe as oxide in the slag. The results obtained a cobalt extraction efficiency of 52% at 950 °C. Further experiments were conducted using pyrite and cobalt sulphide concentrates as sulphating agents which improved the cobalt efficiency to 72% at a 1:1 ratio of slag to pyrite (Mututubanya, 2013). Another study by Altundogan and Tümen (1997) proposed the recovery of Cu, Co, Ni and Zn by roasting with ferric sulphate at 500 °C followed by water leaching. The results show that ferric sulphate caused sulphation of copper slag constituents, producing recovery levels of 93%, 38%, 13% and 59% for Cu, Co, Ni and Zn respectively.

Sukla et al. (1986) studied roasting of copper converter slag using sulphuric acid and achieved recoveries for Cu, Ni and Co of 95%, 90% and 99%, respectively. It was observed that the Fe contamination was 60–80% and removal of most of the Fe from the leach liquors was achieved with ammonia liquor and lime as precipitants, bringing the Fe level to about 3%. In a similar study, the recovery of Cu, Co and Zn from copper smelter and converter slags by roasting with sulphuric acid was conducted (Arslan and Arslan, 2002). The study investigated the effects of roasting time, roasting temperature, and acid/slag ratio. Metal extractions of 88% of Cu, 87% Co, 93% Zn and 83% Fe were achieved after two hours of roasting at 150 °C and with a 3:1 acid/slag ratio. The authors observed that increasing the roasting time to four hours further increased the extraction of copper to 95%. However, high iron content makes further treatment of the leach liquor unfavourable. Recent studies have shown that increasing the sulphation temperature could reduce the

iron content in the leach liquor (Dimitrijevic et al., 2016). The method involved roasting the slag in the presence of sulphuric acid at an initial temperature of 250 °C, thus achieving maximum copper extraction efficiency of about 94% with iron dissolution of 55%. When further experiments were carried out by roasting at a much higher temperature of 600 °C, the iron extraction efficiency was reduced to about 6%, however the copper recovery was also reduced to 79%.

Other methods have involved roasting the copper slag by combining sulphuric acid with ammonium sulphate (Sukla et al., 1986). This study was carried out by roasting the slag at 150 °C, leading to sulphation of the metals of interest. The leaching was conducted in water in an agitated system using a particle size of $\sim 150 \mu\text{m}$. The use of ammonium sulphate in the roasting was found to be effective and maximum copper recovery levels of over 80% were obtained. Rudnik et al. (2009) explored the roasting of slag in reducing conditions to produce Cu–Co–Fe–Pb alloy, and thereafter electrolytic dissolution of the alloy in an ammonium chloride solution was conducted. The results indicated that 99.9% high purity copper was deposited while cobalt recovery of 92.0% was obtained during the selective electrowinning process. A study was conducted by Bulut (2006) on the reduction of slag using graphite in a DC arc furnace and thereafter the reduced slag was leached in hot sulphuric acid giving extraction efficiencies of 78% of the Cu and 90% of the Co. The preliminary conversion of Cu and Co to Cu_2S and CoS from the copper slag using H_2S gas has been shown to attain high extraction efficiencies for copper and cobalt metals (Ziyadnogullari, 1992). The recoveries after roasting and leaching with agitation in water at a particle size of $149 \mu\text{m}$ were 100% of the Cu and 70.7% of the Co. Deng and Ling (2007) demonstrated that thermal acid aging followed by water leaching was an effective method for recovery of metal values from copper slag giving an extraction efficiency of 93% of the Cu.

Treatment using ammonia chloride at 320 °C for 120 min followed by water leaching was investigated to recover the metal values from smelter slag (Nadirov et al., 2013). Extraction efficiencies of 89.7%, 91.5%, and 88.3% for Cu, Zn and Fe respectively were obtained. The authors observed that the recovery of iron to a water-soluble form was more temperature dependant than the processes of zinc and copper recovery. Metal hydroxides were selectively precipitated from the solution by varying the pH of the solution.

4. Copper slag as construction material

The construction industry is an example of an industry that is seeking to reduce its carbon footprint by using recycled materials for construction (Ravindra et al., 2017). One opportunity is the use of secondary materials arising from copper slag waste. Copper slag has been reported to possess favourable physical and mechanical properties such as abrasion resistance and high stability which has attracted interest for the production of blended cements, pavement, abrasives, concrete, tiles, glass, cutting tools and roofing granules (Gorai et al., 2003). The use of copper slag in the concrete industry as a partial replacement for cement and/or fine aggregates could potentially reduce environmental harm and also reduce the costs of slag disposal (Mobasher et al., 1996; Alp et al., 2008; Al-Jabri et al., 2011).

The cementitious properties of copper slag have been considered for blended cementitious mixtures (Mobasher et al., 1996; Tixier et al., 1997), fine aggregate for concrete (Akihiko and Takashi, 1996; Wu et al., 2010b; Sharma and Khan, 2017), admixtures in concrete and mortars (Moura et al., 1999), as an iron source (Huang, 2001; Shi et al., 2008; Alp et al., 2008), cementitious materials for cement mortars (Al-Jabri et al., 2002), pozzolanic supplementary cementing material (Moura et al., 2007), sand substitution (Al-Jabri et al., 2009; Wu et al., 2010a), protection against sulphate attack (Najimi et al., 2011), fine aggregates (Al-Jabri et al., 2011), alternative to river sand (Mithun and Narasimhan, 2016), structural fill (Prasad and Ramana, 2016), aluminosilicate material (Singh and Singh, 2019), and supplementary cementitious material (Feng et al., 2019). Research has also considered

the potential use of copper slags for fabrication of unglazed floor tiles (Marghussian and Maghssoodipoor, 1999), supplements for treating soft marine clay (Chew and Bharati, 2009) and infill for electromagnetic interference shielding materials (Fan et al., 2018).

4.1. Copper slag for Portland cement

Several studies have investigated the use of copper slag waste as a pozzolanic material for partial replacement of ordinary Portland cement, including its effects on the properties of mortar and concrete (Mobasher et al., 1996; Al-Jabri et al., 2002 and 2006; Sanchez et al., 2004; Ueno et al., 2005; Moura et al., 2007; Chew and Bharati, 2009; Najimi et al., 2011; Prasad and Ramana, 2016; Mithun and Narasimhan, 2016; Fan et al., 2018; Feng et al., 2019; Singh and Singh, 2019). A pozzolanic material is a material which gains cement-like properties when reacted with calcium hydroxide.

Mobasher et al. (1996) investigated the effect of copper slag on the hydration of cement-based materials. Portland cement was replaced with 15% copper slag by weight of cement and with up to 1.5% of hydrated lime as an activator for pozzolanic reactions. The study found a significant increase in compressive strength for up to 90 days of hydration as well as an increase in gel porosity and a decrease in capillary porosity. This use of copper slag had the dual benefits of lowering the cost of the concrete and eliminating the disposal costs. Moura et al. (2007) also proposed the use of copper slag as pozzolanic supplementary cementing material. The study investigated the specific gravity, compressive strength, splitting-tensile, absorption rate by capillary suction and carbonation of the product after the addition of 20% of copper slag to concrete batches. The results indicated that the addition of copper slag to concrete batches improved the mechanical and durability performance. Al-Jabri et al. (2002) reported that the highest 90 days compressive strength of up to 42 MPa can be achieved with the use of copper slag and cement by-pass dust as replacements on cement mortars. The samples met the required number of days for compressive strength specifications for cement mortars.

Copper slag has been also found to be effective in treating soft marine clay as a partial substitute for cement (Chew and Bharati, 2009). The findings demonstrated that the workability and the unconfined compressive strength of cement-treated clay remained constant with or without copper slag. Prasad and Ramana (2016) explored the feasibility of copper slag as a structural fill for mechanically stabilised earth walls and reinforced soil slopes in place of conventional fill materials. The chemical, physical, electrochemical, and interfacial frictional characteristics of copper slag and conventional fill material were investigated. The physical, gradation, shear strength and electrochemical characteristics of copper slag were found to be analogous to most of the standard specifications for a backfill material recommended for use in mechanically stabilised earth walls and reinforced soil slopes. The authors concluded that copper slag can be used effectively as a structural fill for mechanically stabilised earth walls and reinforced slopes.

Fan et al. (2018) reported that copper slag has competitive economic and social benefits as an in-fill for electromagnetic interference shielding materials. The addition of 45 wt% of copper slag to the cement matrix boosted the shielding effectiveness to about 8 dB in the frequency range of 0.5 to 1.5 GHz. A recent study by Feng et al. (2019) revealed that mechanical activation using vibratory milling enhanced the pozzolanic activity of granulated copper slag making it a suitable supplementary cementitious material. Ueno et al. (2005) suggested a grading distribution of fine aggregate based on particle density, in order to control the bleeding in concrete mixtures when incorporating copper slag as fine aggregates. The study investigated the maximum size of copper slag fine aggregate that does not significantly influence the amount of bleeding, and the required plastic viscosity of paste to control the amount of bleeding by the variation of water-to-cement ratios.

A study was conducted on the use of copper slag as an alternative to river sand as fine aggregate in alkali-activated slag concrete mixes for

structural applications (Mithun and Narasimhan, 2016). The mixture was compared to a conventional Portland cement concrete mix in terms of the workability, strength and durability parameters. The results indicated that the mixture of alkali-activated concrete with copper slag as a replacement for sand for up to 100% by volume showed comparable strength characteristics and modulus of elasticity, with lower total porosity, reduced water absorption and chloride ion penetration. Similarly, Singh and Singh (2019) conducted a feasibility study on the use of copper slag as an aluminosilicate material for developing alkali-activated cementitious material. The addition of fly ash and metakaolin mineral admixtures on the performance of alkali-activated copper slag was also investigated. The admixtures were activated using sodium hydroxide and sodium silicate. The results demonstrated that the addition of 100% copper slag had good performance. The addition of fly ash and metakaolin in alkali-activated copper slag makes it even more effective as a cementitious material for the construction industry.

4.2. Copper slag for cement clinker production

Copper slag waste has been used to adjust iron during cement clinker production due to its high iron content (Huang, 2001). The main constituent of the copper slag used by Huang (2001) was vitreous ferrosilite (FeSiO_3) which has a low melting point and could be used to significantly reduce the calcination temperature for cement clinker production. The replacement of iron powder with copper slag was found to reduce or eliminate the need for mineraliser (Shi et al., 2008). The cement produced using copper slag waste performed better than that using iron powder. The potential use of flotation waste copper slag as an iron source in the production of Portland cement clinker has been reported (Alp et al., 2008). The clinker products obtained using copper slag from the industrial scale trial operations were characterised and the physico-mechanical performance of the resultant cement products was evaluated. The study revealed that the mortar samples obtained using flotation waste copper slag pose no environmental risks, unlike the untreated slag which is a potential source of heavy metal contamination. The findings suggested that utilisation of flotation waste copper slag as a raw material for cement could reduce production costs for cement raw materials due to its availability in large quantities, with the further significant benefits for slag waste management.

4.3. Copper slag for aggregate in concrete

Copper slag possesses mechanical characteristics such as low porosity and high hardness which makes it suitable to be used as alternative to natural sand and/or as a substitute for aggregates in concrete. Furthermore, copper slag exhibits pozzolanic properties due to its low CaO content as well as other oxides such as Al_2O_3 , SiO_2 , and Fe_2O_3 (Al-Jabri et al., 2011). Several studies have investigated the properties of concrete made with copper slag waste and have shown that the use of copper slag can improve the strength, durability, deformation, and permeability properties of concrete (Ravindra et al., 2017).

Akihiko and Takashi (1996) reported the use of copper smelter slag as a fine aggregate in concrete. The effects of using several types of slag on mortar and concrete reactions, reinforcing steel corrosion, abrasion, shrinkage, workability and slump characteristics were investigated. Copper slag waste has been considered as a potential alternative to admixtures used in concrete and mortars (Moura et al., 1999). The performance of high strength concrete made using copper slag as a fine aggregate was investigated by Al-Jabri et al. (2009). The study involved variation of copper slag proportions and adjusting the amount of water in each mixture to achieve constant workability. The findings demonstrated that the use of copper slag as a substitute for sand improved the strength and durability of high strength concrete at the same workability. In a follow-up study by Al-Jabri et al. (2011), it was found that replacing up to 50% by weight of sand with copper slag produced concrete with good strength and durability requirements. Various mortar

and concrete mixtures were prepared with different proportions of copper slag ranging from 0% to 100% of the fine aggregate. The fatigue life of a bituminous mix made with copper slag was found to be higher than the ones made with natural sand alone (Al-Jabri et al., 2011). Ravindra et al. (2017) found that the use of copper slag in bituminous mix makes it less susceptible to moisture damage and increases the workability and the compressive strength of admixtures used in concrete for a given cement to water ratio.

While there are several benefits of using copper slag as fine aggregates, settling time has been found to be one of the negative effects (Ayano and Sakata, 2000). It was observed that there were longer setting times for the small particle sizes typical of copper slag. To overcome this, the washing time was increased. The study concluded that the tensile and compressive strengths of concrete specimens made with copper slag fine aggregates were the same as that of normal concrete, and even greater than control mixtures. In a similar study, Wu et al. (2010a) investigated the mechanical properties of high strength concrete incorporating copper slag as a fine aggregate. The study assessed the workability and strength characteristics through a series of tests using 20% incremental increases in copper slag replacement of sand up to 100%. The results indicated that for less than 40% copper slag replacing sand, a high strength concrete was achieved which was comparable to or better than the control specimen. The sustainable use of copper slag as fine aggregates in self compacting concrete using fly ash and silica fume as supplementary cementitious materials has been explored (Sharma and Khan, 2017). The self-compacting concrete mix with 100% copper slag as fine aggregates was found to be more cost effective, with low embodied energy. The results indicate that copper slag in combination with supplementary cementitious materials is a promising alternative to conventional sand in the construction industry. The study by Wu et al. (2010b) investigated the mechanical properties of copper slag reinforced concrete under dynamic compression. The findings demonstrated that the dynamic compressive strength of reinforced concrete generally improved with an increase in the amounts of copper slag replacing sand up to 20%, compared with the control concrete.

4.4. Copper slag for road pavement

The effect of copper slag on the engineering properties of road pavements has been described in the literature. Copper slag is a viable replacement material for natural aggregates in the construction of road pavements. A pavement consists of multiple layers of road construction materials such as soils and/or aggregates as main components. The multiple layers in a pavement generally consist of subgrade, capping layer, subbase, base course, binder course and/or surface course. The engineering performance of the aggregate used in all the pavement layers increases from the subgrade to the surface course, suggesting that a wide range of road construction materials with different properties can be used. Copper slag can potentially be used in different pavement layers, but it has mainly been considered for upper layers such as bituminous bound and hydraulically bound applications. Copper slag increases workability, compressive and flexural strengths, and decreases drying shrinkage of road pavement concrete when used in hydraulically bound applications (Ravindra et al., 2017). The repetitive nature of traffic loading can lead to degradation of layers of a flexible pavement (bituminous bound upper layers) under applied tensile stress. This progressive fracture can weaken the durability of a pavement by allowing the permeation of water and air leading to total pavement failure. Therefore, the fatigue life on the specimen can be assessed to determine the number of load applications required before failure. Dawson et al. (2012) investigated the fatigue life of bituminous bound mixes made with 80% copper slag and limestone aggregate. The results showed that the fatigue life of the bituminous bound mix made with 80% copper slag was higher than that made from limestone aggregate. In a similar study by Ravindra et al. (2017), the fatigue life of bituminous bound mix made with copper slag was found to be higher than that made from natural sand and while retaining the same water sensitivity.

The presence of water can weaken the bond that is formed between bitumen and aggregate particles in a bituminous bound mix, causing separation of the bitumen adhering to the aggregate. This moisture damage reduces the strength and integrity of the pavement. The Authors further observed that the use of copper slag reduces the modulus of bituminous mix associated with its smooth surface and low bitumen absorption properties. In another study, the friction and cohesive qualities of copper slag used as aggregate in asphalt mixes containing reclaimed asphalt pavement has been investigated (Raposeiras et al., 2016). The results demonstrated that the use of about 35% of copper slag significantly increased the flow values and decreased the stability values, making copper slag a promising additive to reclaimed asphalt pavement.

5. Environmental factors of copper slags

The environmental impact of slags is closely related to their potential of releasing hazardous elements to the environment. There is evidence of slag accumulations in various parts of the world due to extensive mining activities which date back to pre-historic times. In the past, slags were considered to be inert materials due to limited knowledge, and the life cycle was typically restricted to production and dumping. For this reason, the historical industrial areas have had no integration plan for remediation, recycling, and repurposing of copper slags. In recent years, the disposal of slag wastes has become one of the rising environmental concerns. Therefore, the mining industry is now faced with stringent environmental legislation which requires safe disposal and regular environmental monitoring of dumping sites to prevent the deterioration of the environmental quality.

5.1. Weathering of copper slag

One of the approaches for determining the environmental impacts of copper slag involves analysis of mineral phase alteration due to weathering. Weathering is the process that alters the chemical and mineralogical composition of the slag leading to formation of secondary mineral phases. This involves physical alteration such as disintegration of mineral phases caused by change in temperature and wind whereas the chemical alteration may involve the oxidation and reduction processes. Ettler et al. (2003) noted that the analysis of mineral phase alteration allows prediction of conditions favourable for the mobilisation and immobilisation of metals, and secondary phase formation. The study observed that the presence of some metal-bearing phases showing relatively high susceptibility to alteration was found to potentially increase the risk of metal mobilisation from slags. Therefore, the distribution of metallic elements in various phases of the copper slag wastes constitutes a significant factor governing mobilisation of these elements during weathering. In a similar study, Piatak et al. (2014) has shown that secondary phases formed from slag weathering are an indication of the reactivity of the material which could potentially release toxic elements into the environment. A comprehensive review by Potysz et al. (2015) indicated that the weathering of slag occurs at different rates, the extent of the weathering processes depends on a number of conditions such as chemical, and mineralogical properties of the slag, the physicochemical conditions, the environment, and presence of microorganisms. The study noted that the environmental risk does not necessarily mean the potential release of hazardous compounds by metal-bearing phases. This is because some phases may be resistant to weathering and could be considered as low influential mineral phases to the environment. Conversely, some phases can easily be weathered in a given condition and should be considered as harmful to the environment. Several studies have shown that the metal sulphides are the most susceptible to weathering conditions as they can easily be altered, particularly under oxidising conditions which may increase the potential risk of metal mobilisation (Parsons et al., 2001; Ettler et al., 2009; Potysz et al., 2015). In this perspective, it is important to account for both the total metal concentration and the phase composition to understand the weathering behaviour of slags.

5.2. Environmental risk assessment of copper slag

It is increasingly necessary to assess the potential environmental risks arising from copper slags by conducting tests on the leaching of heavy metals. Studies have been conducted using leaching tests in order to ensure that the material does not have negative environment impacts and is non-hazardous. Concentrations of metals in the leach solutions have found to provide insights into the potential metal content that can be released into the environment, whilst the calculated relative quantities of inorganic components in solution also give information on the susceptibility of slag to weathering (Piatak et al., 2004; Ettler et al., 2009; Kierczak et al., 2013; Piatak et al., 2014; Potysz et al., 2015). The studies have shown that copper slags contain toxic elements which may be responsible for surface water, soil and groundwater pollution (Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2009; Piatak et al., 2014; Potysz et al., 2018). The contamination of soil and water sources due to slag leachate is linked to different types of diseases such as anaemia, and lung and stomach cancer as well as irreparable skin and respiratory disorders when over-exposed (Vestola et al., 2010). In a separate study, the extensive intake of iron can cause hemochromatosis: the disease which damages the tissues in the human body due to the iron accumulation (Kumar et al., 2006). Further, the release of these potentially toxic elements to the environment may lead to loss of biodiversity (Kambole et al., 2019). Piatak et al. (2014) observed that the concentrations of some elements in the copper slag were way above the United States Environmental Protection Agency (USEPA) standard soil screening levels for human contact based on multiple exposure pathways.

However, the use of copper slag in the concrete industry as a partial replacement for cement and/or fine aggregates has been found to potentially reduce the environmental harm, lower the cost of concrete, and eliminate the cost of slag disposal (Mobasher et al., 1996; Alp et al., 2008; Al-Jabri et al., 2011; Ravindra et al., 2017). Zain et al. (2004) found that mortar with copper slag waste replacing up to 10% of cement was safe according to standards with respect to leachability of heavy metals. In another study, Najimi et al. (2011) observed that partial replacement of cement with copper slag was an effective method for improving concrete resistance to sulphate attack. The experimental study investigated expansion measurements, compressive strength degradation and microstructural analysis of concretes in a sulphate solution for various proportions of copper slag. These results are supported by Sanchez et al. (2004) who reported that copper slag incorporation into cement mortar does not cause an increase in the leached elements. Although several of these studies have focused on the physical and mechanical properties of copper slag as a partial replacement for Portland cement and/or fine aggregates, comparatively little attention has been paid to the leaching characteristics of the trace elements present in the iron silicate copper slag either as metal particles, chemically dissolved oxide, or tiny mechanically entrapped sulphide matte. To address potential leaching damage from the trace elements, Holland et al. (2019) proposed a method of upgrading copper slag tailings to have a low impurity content. The study focused on reduction at low temperatures for transforming magnetite into metallic iron and removing high vapour pressure impurities into the gas phase. The results indicated that a complete transformation of magnetite was achieved within the first 30 min of the process. Additionally, fractions of harmful impurities present in the copper slag such as antimony, arsenic, bismuth, lead and zinc were removed from the slag as flue dust in the process off-gas (Holland et al., 2019). However, the method of testing on the toxicity characteristic leaching procedure developed to simulate leaching in a weakly acidic environment by the USEPA found that the leached element concentrations in copper slag were below the maximum allowable limit (Ravindra et al., 2017). These observations could have been attributable to significantly lower amounts of leached elements in the copper slag waste than the regulatory levels determined by the USEPA. Overall, copper slag waste is considered to be a non-hazardous material when used in construction according to the report by the USEPA of 1991 (Ravindra et al., 2017) and these findings were confirmed by an independent organisation, the Basel Convention of 1996 (Alter, 2005).

6. Conclusions

An overview of the chemical and mineralogical composition of copper slags from the 21 major producing countries has shown that copper slags are highly heterogeneous and chemically diverse due to the variation in raw materials, furnaces and cooling conditions. Thus, characterisation of the copper slag is fundamentally important in developing the best approach for metal recovery, assessing the environmental impacts, and slag utilisation as a construction material. The average chemical composition indicates that copper slag consists predominantly of SiO_2 , FeO , Fe_2O_3 , and small amounts of CaO , and Al_2O_3 as well as metals such as Cu, Co, Ag, Ni, Zn, Pb, Cd, and Fe in oxide, or sulphide and/or metallic forms.

The recovery of metal values is of particular importance because copper slag contains significant amounts of residue metals with average of 1.83 wt% of Zn, 1.67 wt% Ag, 1.36 wt% Mg, 1.19 wt% Cu, 0.94 wt% Pb, and 0.48 wt% Co. The review of the various copper slag processing strategies has shown that extensive research has been conducted using flotation, pyrometallurgy, hydrometallurgy and pyro-hydrometallurgy methods. The pyro-hydrometallurgy technique involving roasting followed by water or acid leaching is by far the most common method. Although high metal extraction efficiencies have been reported using sulphuric acid as a leaching or roasting agent, the high consumption of acid and lime, as well as poor filtration characteristics due to formation of iron hydroxide precipitates and silica gel, limits the practicality of the process. Undoubtedly, a more nuanced approach for extraction of valuable metals from copper slag is needed to scale up from laboratory-based tests to industrial application. These discussions are useful and would inform a research dialogue in understanding copper slag processing dynamics and development of an efficient technology.

Review of studies on the utilisation of copper slag as a construction material shows that the physico-mechanical characteristics of copper slag makes it suitable for production of Portland cement, cement clinker, concrete, and road pavement. Copper slag has better performance than ordinary Portland cement when used as a cement or aggregate replacement and has the potential to reduce the energy requirement and lower the carbon footprint. Further, utilisation of copper slag in cement clinker production has the benefits of replacing iron powder as an iron adjusting material and eliminating the mineraliser. Generally, the use of copper slag as a partial replacement for cement and/or fine aggregates eliminates the cost of slag disposal, minimises the cost of concrete and reduces the impacts on the environment.

In recent years, stringent environmental regulations, limited availability of disposal sites, and waste management costs have heightened attention to development of a sustainable solution for the management of slag wastes. The current waste management guidelines recommend sustainable processing strategies of produce, use, and recycle. In this regard, rather than dumping the copper slag waste, the recovery of metal values, recycling, and utilisation are undoubtedly the most promising options for sustainable management of these wastes. Overall, copper slag shows great potential as a material whose processing can lead to a circular economy and more sustainable society.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank the Schlumberger Foundation Faculty for the Future Fellowship for the financial support.

Appendix A

(see Table 4a and Table 4b)

Table 4a
Chemical Composition of copper slag by country.

Author	Country	Cu	Co	Ni	Pb	Zn	Fe	Al	Mg	Mn	Mo	Ti	Ca	As	Sb	Si	Fe ₂ O ₃	FeO	Al ₂ O ₃	CaO	MgO	MnO	SiO ₂	TiO ₂	K ₂ O	P ₂ O ₅	Na ₂ O	S
Lotermoser, 2002 ¹	Australia	0.52	–	–	0.76	2.36	–	–	–	–	–	–	–	0.03	–	–	–	32.88	5.41	15.53	0.91	0.39	34.80	–	0.60	0.27	0.26	1.15
Lotermoser, 2002 ²	Australia	0.63	–	–	0.02	4.79	–	–	–	–	–	–	–	–	–	–	–	31.72	3.12	15.46	1.72	0.45	35.77	–	0.27	0.12	0.04	1.05
Lotermoser, 2002 ³	Australia	0.86	–	–	0.01	5.86	–	–	–	–	–	–	–	–	–	–	–	43.66	3.46	9.12	0.85	0.56	28.70	–	0.03	–	–	1.35
Gbor et al., 2006	Canada	0.75	0.18	0.69	–	–	32.31	–	–	–	–	–	–	–	–	17.00	–	–	–	–	–	–	–	–	–	–	–	–
Gbor et al., 2003	Canada	0.58	0.21	–	–	–	37.00	2.50	1.70	–	–	–	1.10	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.93
Herreros et al., 1998 ¹	Chile	1.61	–	–	–	–	35.80	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Herreros et al., 1998 ²	Chile	1.22	–	–	–	–	32.24	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Imris et al., 2000	Chile	0.79	–	–	–	–	41.53	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	37.13	–	–	–	–	0.11
Gonzalez et al., 2005 ¹	Chile	0.90	–	–	–	–	41.20	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Gonzalez et al., 2005 ²	Chile	1.10	–	–	–	–	43.40	–	–	–	0.30	–	–	–	–	14.00	–	–	–	–	–	–	–	–	–	–	–	–
Carranza et al., 2009	Chile	0.78	–	–	–	–	32.80	–	–	–	0.30	–	–	–	–	14.40	–	–	–	–	–	–	–	–	–	–	–	–
Busolic et al., 2009 ¹	Chile	1.19	–	–	–	–	43.00	–	–	–	0.40	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Caraso et al., 2011	Chile	0.72	–	–	–	1.49*	–	–	–	–	–	–	–	–	–	–	3.95	–	–	0.90	0.84	–	28.07	–	–	–	–	0.84
Busolic et al., 2009 ²	Chile	1.32	–	–	–	–	50.70	–	–	–	0.20	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Wang et al., 2013	Chile	0.87	0.02	–	0.03	0.20	41.70	1.45	0.56	0.02	0.12	0.37	0.05	0.02	0.03	13.60	–	–	–	–	–	–	–	–	–	–	–	0.43
Yang et al., 2010	China	1.35	4.09	0.04	1.16	1.70	28.43	3.22	2.15	0.14	0.01	0.19	5.13	–	–	15.38	–	–	–	–	–	–	–	–	–	–	–	0.11
Fan et al., 2017	China	1.22	0.43	–	0.12	0.49	40.72	2.21	–	–	–	–	3.13	–	–	15.48	–	–	–	–	–	–	–	–	–	–	–	0.40
Guo et al., 2018 ¹	China	0.65	0.01	0.03	0.28	1.11	40.33	–	–	–	–	–	–	0.10	–	–	–	39.85	–	1.10	1.96	–	32.33	–	–	–	–	1.40
Guo et al., 2018 ²	China	2.71	–	0.48	0.68	1.98	39.56	–	–	–	–	–	–	0.04	–	–	–	–	3.71	2.50	1.05	–	26.61	–	–	–	–	0.83
Banza et al 2002	Congo	1.43	0.72	–	–	8.90	20.70	2.56	2.53	–	–	–	6.26	–	–	15.37	–	–	–	–	–	–	–	–	–	–	–	0.59
Tshiongo et al 2010	Congo	0.20	1.70	–	0.9*	5.00	27.00	–	–	–	–	–	–	–	–	–	–	–	6.00	8.60	5.60	–	32.00	–	–	–	–	0.40
Tümen & Bailey,1990	England	3.40	–	0.48	–	–	21.90	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Kaksonen et al 2016	Finland	0.38	0.05	0.04	0.60	2.79	40.90	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
kaksonen et al 2017	Finland	0.38	0.04	0.05	0.60	2.79	40.90	–	–	–	–	–	–	0.16	0.04	–	–	–	–	–	–	–	29.60	–	–	–	–	0.14
Jalkanen et al., 2003 ¹	Finland	1.50	–	–	–	–	–	–	–	–	–	–	–	0.20	0.07	–	–	–	–	–	–	–	–	–	–	–	–	0.13
Jalkanen et al., 2003 ²	Finland	1.70	–	–	–	–	–	–	–	–	–	–	–	0.20	0.07	–	–	–	–	–	–	–	–	–	–	–	–	0.17
Manase & Mellini, 2002 ¹	Italy	0.40	–	–	0.17	1.16	33.97*	–	–	–	–	–	–	–	–	–	–	–	6.48	10.66	2.19	0.74	39.58	0.24	1.73	0.20	0.04	1.66
Manase & Mellini, 2002 ²	Italy	0.38	–	–	1.16	2.23	38.28*	–	–	–	–	–	–	–	0.14	–	–	–	7.37	20.34	1.70	0.86	23.07	0.38	1.55	0.24	0.09	0.69
Manase & Mellini, 2002 ³	Italy	0.32	–	–	0.59	0.42	55.71*	–	–	–	–	–	–	–	0.14	–	–	–	5.98	13.28	1.10	0.23	15.93	0.28	1.11	0.24	0.12	4.07
Addis et al, 2016	Italy	1.48	–	–	0.18	–	–	–	–	–	–	–	–	–	–	–	54.17	–	5.32	4.20	2.81	0.22	28.04	0.20	0.93	0.15	0.08	1.13
Anand et al 1980	India	1.76	0.19	0.23	–	–	46.46	–	0.97	–	–	–	2.09	–	–	–	–	–	1.58	–	–	–	33.57	–	–	–	–	–
Agrawal et al., 2000 ¹	India	0.60	0.13	0.06	–	–	44.00	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	28.00	–	–	–	–	–
Agrawal et al., 2000 ²	India	0.73	–	0.00	–	0.23	46.20	–	–	–	–	–	–	–	–	–	–	–	–	2.75	–	–	–	–	–	–	–	0.60
Agrawal et al., 2000 ³	India	0.70	–	–	–	–	41.53	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	29.90	–	–	–	–	–
Agrawal et al., 2000 ⁴	India	0.68	0.22	0.05	–	0.05	47.13	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.47
Das et al, 2010	India	1.53	0.04	0.02	–	–	39.80	–	–	0.34	–	–	–	–	–	–	55.10	0.71	2.30	3.95	2.82	–	30.91	–	–	–	–	1.24
Subrata et al 2015	India	1.90	–	–	–	–	51.58	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ambily et al, 2015	India	1.2*	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.22	0.15	–	0.22	25.84	0.41	0.23	–	0.58	0.25
Roy et al, 2015	India	1.90	–	–	–	–	–	–	–	–	–	–	–	–	–	12.15	–	–	–	–	–	–	–	–	–	–	–	–
Prasad & Ramana, 2016	India	1.49*	–	–	0.09*	1.55*	–	–	–	–	–	–	–	–	–	–	61.24	–	3.03	5.65	0.90	0.08	19.72	0.44	1.23	0.63	–	–
Sharma & Khan, 2017	India	0.64*	–	–	–	–	–	–	–	–	–	–	–	–	–	–	57.82	–	2.80	1.60	1.48	–	30.53	0.26	0.71	–	0.34	–
Meshram et al 2017	India	0.53	0.03	0.01	–	–	44.09	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	11.09	–	–	–	–	–
Gupta & Siddique, 2020	India	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	55.60	3.65	3.31	1.51	–	33.62	–	0.82	–	0.37	–

-Data not provided, *reported in oxide form. ^{1 2 3 4} mine cites/types of slag

Table 4b

Chemical Composition of copper slag by country.

Author	Country	Cu	Co	Ni	Pb	Zn	Fe	Al	Mg	Mn	Mo	Ti	Ca	As	Sb	Si	Fe ₂ O ₃	FeO	Al ₂ O ₃	CaO	MgO	MnO	SiO ₂	TiO ₂	K ₂ O	P ₂ O ₅	Na ₂ O	S
Marghussian & Maghsoodipoor, 1999	Iran	–	–	–	–	–	44.78	–	–	–	–	–	–	–	–	–	–	–	3.78	5.24	1.16	–	40.97	–	–	–	–	1.06
Shamsi et al 2015	Iran	0.98	–	–	–	–	–	–	–	–	–	–	–	–	–	–	6.85	–	15.89	9.02	3.45	0.11	51.34	0.59	5.94	0.25	3.25	–
Khanzadi & Behnood, 2009	Iran	1.2*	–	–	–	0.84*	–	–	–	–	–	–	–	–	–	–	52.50	–	7.80	4.60	1.20	–	27.80	0.49	1.60	–	–	–
Nadirov et al., 2013	Kazakhstan	2.20	–	–	–	5.92	36.41	0.74	–	–	–	2.94	–	–	–	15.30	–	–	–	–	–	–	–	–	–	–	–	1.34
Nadirov et al., 2017	Kazakhstan	1.18	–	–	–	4.57	39.70	1.54	0.18	–	–	0.77	–	–	–	13.95	–	–	–	–	–	–	–	–	–	–	–	1.06
Nadirov & Mussapyrova, 2019	Kazakhstan	1.20	–	–	–	4.52	13.88	1.49	0.18	–	–	0.76	–	–	–	39.79	–	–	–	–	–	–	–	–	–	–	–	1.11
Huanosta-Gutierrez et al., 2012	Mexico	1.40	–	–	–	–	36.00	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Maldonado, 2006	Mexico	1.509*	–	–	0.048*	0.099*	39.77*	–	–	–	–	–	–	–	–	–	–	–	7.30	1.66	1.29	0.08	45.41	0.22	1.06	0.06	0.44	–
Ettler et al 2009	Namibia	2.75	0.02	0.01	10.39	2.82	32.47	–	–	–	–	–	–	2.41	0.22	–	32.47	9.49	4.70	4.50	1.43	0.08	14.68	0.25	0.30	0.59	0.26	6.51
Potysz et al 2018	Poland	0.41	–	–	0.01	0.02	–	–	–	–	–	–	–	–	–	–	4.76	–	17.60	18.10	2.73	0.21	46.50	0.80	5.97	–	0.19	–
Potysz et al., 2016 ¹	Poland	0.57	0.04	–	0.01	0.40	–	–	–	–	–	–	–	–	–	–	50.70	–	7.46	1.10	2.50	0.17	37.60	0.45	1.58	–	0.27	0.67
Potysz et al., 2016 ²	Poland	1.14	0.10	0.04	2.10	0.78	–	–	–	–	0.07	–	–	0.09	–	–	16.42	–	10.05	20.93	5.73	0.24	32.60	0.58	3.02	–	0.79	less than 0.02
Kierczak and Pietranik, 2011	Poland	1.14	–	–	0.78	2.11	51*	–	–	–	–	–	–	–	–	–	–	–	–	–	–	70.00	–	–	–	–	–	–
Potysz et al., 2017	Poland	1.10	–	–	2.10	0.80	11.50	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Muravyov et al., 2012	Russia	0.56	–	–	–	4.74	43.30	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Urosevic et al 2015	Serbia	0.97	–	–	–	–	39.09	–	–	–	–	–	–	–	–	–	9.39	33.80	3.78	6.00	1.66	–	33.75	–	–	–	–	–
Dimitrijevic et al 2016	Serbia	0.97	–	–	–	–	39.09	–	–	–	–	–	–	–	–	–	9.39	33.80	3.78	6.00	1.66	–	33.75	–	–	–	–	–
Chew & Bharati, 2009	Singapore	1.02	–	–	0.10	0.80	38.05	2.75	0.78	–	–	5.21	0.19	–	–	13.80	–	–	–	–	–	–	–	–	–	–	–	–
Lottermoser 2006	Spain	0.44	0.03	–	0.21	1.30	45.54*	–	–	0.12	0.01	–	0.01	0.04	–	–	–	45.54	2.61	6.66	0.83	–	–	0.32	–	0.14	–	1.90
Sáez et al, 2003	Spain	3.26	0.01	0.01	0.09	0.02	–	–	–	–	–	–	–	0.19	–	–	12.73	–	10.81	3.70	1.38	2.09	59.27	0.73	2.11	0.95	0.62	0.05
Jones et al 1996	South Africa	0.50	1.00	2.00	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2.00	2.00	1.00	–	30.00	–	–	–	–	1.50
Heo et al, 2016	South Korea	1.8*	–	–	0.1*	1.6*	46.00	–	–	–	–	–	–	–	–	–	–	–	4.80	2.30	1.90	–	27.60	–	–	–	–	1.20
Kim et al, 2013	South Korea	0.70	–	–	0.21	–	51.1*	–	–	–	–	–	–	–	–	–	–	–	4.10	3.40	1.20	–	34.50	–	–	–	–	–
Tümen & Bailey, 1990	Turkey	1.70	0.18	0.04	–	0.14	40.40	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Yucel et al 1992	Turkey	0.82	0.43	0.04	0.07	0.34	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	23.68	–	–	–	–	1.54
Acma et al., 1997 ¹	Turkey	0.83	0.43	0.04	0.07	0.34	56.55	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	23.68	–	–	–	–	1.54
Acma et al., 1997 ²	Turkey	0.82	0.43	0.04	0.07	0.34	56.55	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	23.68	–	–	–	–	1.54
Arslan & Arslan, 2002	Turkey	2.64	0.10	0.07	0.13	0.67	47.20	–	–	–	–	–	–	–	–	8.50	–	–	–	–	–	–	–	–	–	–	–	1.30
Kiyak et al, 1999	Turkey	1.01	0.10	0.02	–	0.72	39.65	–	–	–	–	–	–	–	–	–	–	–	2.40	3.95	2.82	–	31.94	–	–	–	–	–
Bulut, 2006	Turkey	0.98	0.49	–	–	0.23	51.47	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	21.27	–	–	–	–	1.67
Yuksel and Tegin, 2017	Turkey	1.00	0.30	–	–	–	26.65	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.10
Turan et al, 2017	Turkey	3.8*	–	–	–	3.2*	–	–	–	–	–	–	–	–	–	–	51.00	–	3.50	0.70	–	–	32.00	0.10	0.50	–	–	–
Mobasher et al., 1996 ¹	USA	1.64	–	–	–	–	34.62	–	–	0.49*	–	–	–	–	–	–	–	–	14.70	17.42	3.51	–	27.16	–	–	–	–	0.33
Mobasher et al., 1996 ²	USA	2.10	–	–	–	–	44.80	–	–	0.4*	–	–	–	–	–	–	–	–	15.60	10.90	1.70	–	24.70	–	–	–	–	0.28
Piatak et al 2004	USA	1.35	–	–	–	1.02	37.00	4.90	2.00	–	–	4.10	–	–	–	20.28	–	–	–	–	–	–	–	–	–	–	–	–
Sarfo et al 2017	USA	0.50	–	–	0.16	1.77	–	–	–	0.50	–	–	–	–	–	–	43.90	–	5.48	6.65	0.33	–	34.60	–	1.36	–	1.39	–
Banda et al, 2002	Zambia	1.06*	1.83*	–	–	–	33.74*	–	–	–	–	–	–	–	–	–	–	–	7.94	6.96	3.20	0.10	42.25	0.49	–	0.25	–	–
Vítková et al., 2010 ¹	Zambia	1.95	1.25	0.05	0.06	0.12	17.56*	–	–	–	0.02	–	–	–	–	–	–	–	8.25	12.53	4.17	0.06	9.77	–	2.88	–	0.01	0.31
Vítková et al., 2010 ²	Zambia	0.70	0.17	–	–	0.04	23.44*	–	–	–	–	–	–	–	–	–	–	–	5.47	15.47	2.58	0.07	39.00	–	2.21	–	0.19	less than 0.01
Kakengela et al, 2016	Zambia	2.00	1.54	0.05	–	–	20.44	–	–	–	–	–	–	–	–	–	–	–	7.13	5.30	3.27	–	33.28	–	–	–	–	0.27

-Data not provided, *reported in oxide form. ^{1 2 3 4} mine cites/types of slag

References

- Akihiko, Y., Takashi, Y., 1996. Study of utilisation of copper slag as fine aggregate for concrete. *Ashikaya Kogyo Daigaku Kenkyu Shuroku* 23, 79–85.
- Acma, E., Sesigür, H., Addemir, O., Tekin, A., 1997. Processing of Kure (Turkey) copper slag for the recovery of copper and cobalt and the production of gamma Fe₂O₃. *Trans. Indian Inst. Met.* 50 (2–3), 147–151.
- Addis, A., Angelini, I., Nimis, P., and Artioli, G., 2016. Late bronze age copper smelting slags from Luserna (Trentino, Italy): interpretation of the metallurgical process. *University of Oxford, Archaeometry* 58, 1 96–114.
- Agrawal A, Sahu KK, Pandey BD, Premchand., 2000. State of the Art Report on Metallurgical Waste, Report submitted to MOEF by NML Jamshedpur, May 2000: 64-67.
- Alp, I., Deveci, H., Süngün, H., 2008. Utilisation of flotation wastes of copper slag as raw material in cement production. *J. Haz. Mater.* 159 (2), 390–395.
- Alter, H., 2005. The composition and environmental hazard of copper slags in the context of the Basel Convention. *Resour. Conserv. Recycl.* 43 (4), 353–360.
- Altundoğan, H.S., Tümen, F., 1997. Metal recovery from copper converter slag by roasting with ferric sulphate. *Hydrometallurgy* 44 (1–2), 261–267.
- Altundoğan, H.S., Boyrazlı, M., Tümen, F., 2004. A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate. *Minerals Eng.* 17 (3), 465–467.
- Alvarez-Valero, A.M., Perez-Lopez, R., Nieto, J.M., 2009. Prediction of the environmental impact of modern slags: a petrological and chemical comparative study with Roman age slags. *Am. Mineral.* 94 (10), 1417–1427.
- Hooton, R.D., Al-Jabri, K., Taha, R., Al-Ghassani, M., 2002. Use of copper slag and cement by-pass dust as cementitious materials. *Cem. Concr. Aggr.* 24 (1), 7. <https://doi.org/10.1520/CCA10485J>.
- Al-Jabri, K.S., Hisada, M., Al-Oraimi, S.K., Al-Saidy, A.H., 2009. Copper slag as sand replacement for high performance concrete. *Cem Concr Comp* 31 (7), 483–488.
- Al-Jabri, K.S., Al-Saidy, A.H., Taha, R., 2011. Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete. *Constr. Build. Mater.* 25 (2), 933–938.
- Ambily, P.S., Umarani, C., Ravisankar, K., Prem, P.R., Bharatkumar, B.H., Iyer, N.R., 2015. 16 Studies on ultra high performance concrete incorporating copper slag as fine aggregate. *17 Constr. Build. Mater.* 77, 233–240.
- Anand, S., Rao, P.K., Jena, P.K., 1980. Recovery of metal values from copper converter and smelter slags by ferric chloride leaching. *Hydrometallurgy* 5 (4), 355–365.
- Anand, S., Das, R.P., Jena, P.K., 1981. Reduction-roasting and ferric chloride leaching of copper converter slag for extracting copper, nickel and cobalt values. *Hydrometallurgy* 7 (3), 243–252.
- Anand, S., Sarveswara Rao, K., Jena, P.K., 1983. Pressure leaching of copper converter slag using dilute sulphuric acid for the extraction of cobalt, nickel and copper values. *Hydrometallurgy* 10 (3), 305–312.
- Aracena, A., Fernández, F., Jerez, O., Jaques, A., 2019. Converter slag leaching in ammonia medium/column system with subsequent crystallisation with NaSH. *Hydrometallurgy* 188, 31–37.
- Arslan, C., Arslan, F., 2002. Recovery of copper, cobalt and zinc from copper smelter and converter slags [J]. *Hydrometallurgy* 67 (1–3), 1–7.
- Ayano, T., Sakata, K., 2000. In: *Durability of concrete with copper slag fine aggregate*. SP-192, Barcelona, Spain, pp. 141–158.
- Baghalha, M., Papangelakis, V.G., Curlook, W., 2007. Factors affecting the leachability of Ni/Co/Cu slags at high temperature. *Hydrometallurgy* 85 (1), 42–52.
- Banda, W., Morgan, N., Eksteen, J.J., 2002. The role of slag modifiers on the selective recovery of cobalt & copper from waste smelter slag. *Miner. Eng.* 15, 899–907.
- Banza, A.N., Gock, E., Kongolo, K., 2002. Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction [J]. *Hydrometallurgy* 67 (1), 63–69.
- Abdel Basir, S.M., Rabah, M.A., 1999. Hydrometallurgical recovery of metal values from brass melting slag. *Hydrometallurgy* 53 (1), 31–44.
- Beşe, A.V., Ata, O.N., Çelik, C., Çolak, S., 2003. Determination of the optimum conditions of dissolution of copper in converter slag with chlorine gas in aqueous media. *Chem. Eng. Process.: Process Intensificat.* 42 (4), 291–298.
- Beşe, A.V., 2007. Effect of ultrasound on the dissolution of copper from copper converter slag by acid leaching. *Ultrasonics Sonochem.* 14 (6), 790–796.
- Borisov, V.A., D'yachenko, A.N., Kraidenko, R.I., 2011. Reaction of ammonium chloride with the copper (II) sulfide and oxide, and identification of the reaction products. *Russ. J. Gen. Chem.* 81 (7), 1430–1433.
- Boyrazlı, M., Altundogan, H.S., Tümen, F., 2006. Recovery of Metals from Copper Converter Slag by Leaching With K₂Cr₂O₇-H₂SO₄. *Can. Metall. Q.* 45 (2), 145–152. <https://doi.org/10.1179/cmq.2006.45.2.145>.
- Bulut, G., 2006. Recovery of copper and cobalt from ancient slag. *Waste Manage. Res.* 24 (2), 118–124.
- Busolic, D., Parada, F., Parra, R., Ulloa, A., Carrasco, J.C., Palacios, J., Reghezza, A., Caballero, C., Zúñiga, J., Sanchez, M., 2009. Recovery of Molybdenum from Roasted Copper Slags. *Nonferrous Pyrometallurgy, MOLTEEN 2009*. Santiago, Chile.
- Carranza, F., Iglesias, N., Mazuelos, A., Romero, R., Forcat, O., 2009. Ferric leaching of copper slag flotation tailings [J]. *Miner. Eng.* 22 (1), 107–110.
- Chew, S.H., Bharati, S.K., 2009. Use of recycled copper slag in cement e treated Singapore marine clay. In: *Proceedings of International Symposium on Geoenvironmental Eng. ISGE*, Sept 8 to 10, Hangzhou, China, pp. 705e710.
- Das, B., Mishra, B.K., Angadi, S., Pradhan, S.K., Prakash, S., Mohanty, J.K., 2010. Characterisation and recovery of copper values from discarded slag. *Waste Manage. Res.* 28, 561–567. <https://doi.org/10.1177/0734242X09343943>.
- Davenport, W.G.L., et al., 2002. *Extractive Metallurgy of Copper* (4th edition). Chemical, Petrochemical & Process. Elsevier. 1-452.
- Dawson, A.R., Dehdezi, P.K., Hall, M.R., Wang, J., Isola, R., 2012. Enhancing thermal properties of asphalt materials for heat storage and transfer applications. *Road Mater. Pavement Des.* 13 (4), 784–803.
- Deng, T., Ling, Y., 2007. Processing of copper converter slag for metal reclamation. Part I: extraction and recovery of copper and cobalt. *Waste Manage. Res.* 25, 440–448.
- Dimitrijevic, M.D., Urošević, D.M., Janković, Z.D., Milic, S.M., 2016. Recovery Of Copper from Smelting Slag by Sulphation Roasting and Water Leaching. *Physicochem. Probl. Miner. Process.* 52 (1), 409–421.
- Ettler, V., Piantone, P., Touray, J.C., 2003. Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long-term assessment. *Mineral. Mag.* 67 (6), 1269–1283.
- Ettler, V., Johan, Z., Kribeek, B., Sebek, O., Michaljevic, M., 2009. Mineralogy and environmental stability of slags from Tsumeb smelter. *Namibia. Appl. Geochem.* 24 (1), 1–15.
- Fan, J., Li, H., Wei, L., Li, C., Sun, S., 2017. The Recovery of Copper from Smelting Slag by Flotation Process. *Minerals, Metals & Mater. Soc.*
- Fan, Y., Zhang, B., Song, J., Volski, V., Vandenbosch, G.A.E., Muxing Guo, M., 2018. An Innovated Application of Reutilise Copper Smelter Slag for Cement-based Electromagnetic Interference Composites. *Sci. Rep.* 8, 16155. <https://doi.org/10.1038/s41598-018-34680-5>.
- Feng, Q., Zhao, W., Wen, S., 2018. “Surface modification of malachite with ethanediamine and its effect on sulphidisation flotation. *Appl. Surf. Sci.* 436, 823–831.
- Feng, Y., Kero, J., Yang, Q., Chen, Q., Engström, F., Samuelsson, C., Qi, C., 2019. Mechanical Activation of Granulated Copper Slag and Its Influence on Hydration Heat and Compressive Strength of Blended Cement. *Materials* 2019 (12), 772.
- Ghazitabar, A., Naderi, M., Haghsheenas, D.F., 2018. A facile chemical route for synthesis of nitrogen-doped graphene aerogel decorated by Co₃O₄ nanoparticles. *Ceram. Int.* <https://doi.org/10.1016/j.ceramint.2018.09.126>.
- Gbor, P.K., Mokri, V., Jia, C.Q., 2000. Characterisation of smelter slag. *J. Environ. Sci. Health, Part A: Toxic/Hazardous Substances. Environ. Eng.* 35 (2), 147–167.
- Gbor, P.K., 2003. Behavior of cobalt, nickel, copper and iron during aqueous sulphur dioxide leaching of non-ferrous smelter slag. Ph.D. Thesis. University of Toronto.
- Gbor, P.K., Hoque, S., Jia, C.Q., 2006. Dissolution behavior of Fe Co, and Ni from nonferrous smelter slag in aqueous sulphur dioxide. *Hydrometallurgy* 81, 130–141.
- Gonzalez, C., Parra, R., Klenovcanova, A., Imris, I., Sanchez, M., 2005. Reduction of Chilean copper slags: a case of waste management project. *Scand. J. Metall.* 34, 143–149.
- Gorai, B., Jana, R.K., Premchand, 2003. Characteristics and utilisation of copper slag – a review. *Resour. Conserv. Recycl.* 39 (4), 299–313. [https://doi.org/10.1016/S0921-3449\(02\)00171-4](https://doi.org/10.1016/S0921-3449(02)00171-4).
- Gulay, B., 2006. Recovery of copper and cobalt from ancient slag. *Waste Manage. Res.* 24, 118–124.
- Guo, Z.Q., Pan, J., Zhu, D.Q., Zhang, F., 2018. Co-reduction of copper smelting slag and nickel laterite to prepare Fe-Ni-Cu alloy for weathering steel. *JOM* 70 (2), 150–154.
- Gupta, N., Siddique, R., 2020. Durability characteristics of self-compacting concrete made with copper slag. *Constr. Build. Mater.* 247, 118580.
- Hara, Y., Jha, A., 2016. Carbothermic Processing of Copper-Cobalt Mineral Sulphide Concentrates and Slag Waste for the Extraction of Metallic Values. *Sustain. Mineral Energy Sectors* 7, 105–124.
- Heo, J., Chung, Y., Park, J., 2016. Recovery of iron and removal of hazardous elements from waste copper slag via a novel aluminothermic smelting reduction (ASR) process. *J. Clean. Prod.* 137, 777–787.
- Herreros, O., Quiroz, R., Manzano, E., Bou, C., Viñals, J., 1998. Copper extraction from reverberatory and flash furnace slags by chlorine leaching. *Hydrometallurgy* 49, 87–101.
- Holland, K., Eriç, R.H., Taskinen, P., Jokilaakso, A., 2019. Upgrading copper slag cleaning tailings for re-use. *Miner. Eng.* 133, 35–42.
- Huang K., 2001. Use of copper slag in cement production, *Sichuan Cement*, No. 4; p. 25–70.
- Huanosta-Gutierrez T., Dantas, R.F., Ramirez-Zamora R.M., Esplugas, S., 2012. Evaluation of copper slag to catalyze advanced oxidation processes for the removal of phenol in water.
- Imris, I., Rebolledo, S., Sanchez, M., Castro, G., Achurra, G., Hernandez, F., 2000. The copper losses in the slag from the el teniente process. *Canad. Metall. Quarter.* 39 (3), 281–290.
- Jalkanen, H., Vehviläinen, J., Poijärvi, J., 2003. Copper in solidified copper smelter slags. *Scand. J. Metall.* 32 (2), 65–70.
- Jones, R.T., Hayman, D.A., Denton, G.M., 1996. Recovery of cobalt, nickel and copper from slags using DC-Arc furnace technology. *Mintek paper No, International Symposium challenges of process intensification*, Montreal, Canada, p. 8360.
- Kakengela, K.L., Ngúni, C., Siame, J., Mulwanda, J., 2016. Recovery of Cobalt and Copper from Nchanga Mines Slag using Ferrosilicon. *Int. J. Sci. Technol.* 5 No. 11.
- Kaksonen, A.H., Särkijärvi, S., Puhakka, J.A., Peuraniemi, E., Junnikkala, S., Tuovinen, O.H., 2016. Chemical and bacterial leaching of metals from a smelter slag in acid solutions. *Hydrometallurgy* 159, 46–53.
- Kaksonen, A.H., Särkijärvi, S., Puhakka, J.A., Peuraniemi, E., 2017. Junnikkala, S and OH Tuovinen. *Miner. Eng.* 106, 97–101.
- Kambole, C., Paige-Green, P., Kupolati, W.K. Ndambuki, J.M., Adeboje, A., 2019. Comparison of technical and short-term environmental characteristics of weathered and fresh blast furnace slag aggregates for road base applications in South Africa.
- Khanzadi, M., Behnood, A., 2009. Mechanical properties of high-strength concrete incorporating 12 copper slag as coarse aggregate. *Constr. Build. Mater.* 23, 2183–2188.

- Kierczak, J., Pietranik, A., 2011. Mineralogy and composition of historical Cu Slags from the Rudawy Janowickie Mountains. Southwestern Poland. *Can. Mineral.* 49 (5), 1281–1296.
- Kierczak, J., Potysz, A., Pietranik, A., Tyska, R., Modelska, M., Néel, C., Ettler, V., Mihaljević, M., 2013. Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland). *J. Geochem. Explor.* 124, 183–194.
- Kim, B.S., Jo, S.K., Shin, D., Lee, J.C., Jeong, S.B., 2013. A physico-chemical separation process for upgrading iron from waste copper slag. *Int. J. Miner. Process.* 3, 124–127.
- Kiyak, B., Ozer, A., Altundogan, S.H., Erdem, M., Tümen, F., 1999. Cr(VI) reduction in aqueous solution by using copper smelter slag. *Waste Manage.* 19, 333–338.
- Kumar, S., Kumar, R., Bandopadhyay, A., 2006. *Resour. Conserv. Recy.* 48, 301.
- Kuo, Y.-M., Wang, J.-W., Wang, C.-T., Tsai, C.-H., 2008. Effect of water quenching and SiO₂ addition during vitrification of fly ash Part 1: on the crystalline characteristics of slags. *J. Hazard. Mater.* 152, 994–1001.
- Li, Y., Perederity, L., Papangelakis, V.G., 2008. Cleaning of waste smelter slag and recovery of valuable metals by pressure oxidative leaching. *J. Hazard. Mater.* 152, 607–615.
- Lossin, A., 2001. Copper. *Ullmann's Encyclopedia of Industrial Chemistry*. Doi:10.1002/14356007.a07.471.
- Lottermoser, B.G., 2002. Mobilisation of heavy metals from historical smelting slag dumps, north Queensland. *Austr. Mineral. Magaz.* 66 (4), 475–490.
- Lottermoser, B.G., 2006. Evaporative mineral precipitates from the historical smelting slag dump, Rio Tinto. *Spain. J. Mineralogy Geochem.* 181 (2), 183–190.
- Lottermoser, B.G., 2010. *Mine Wastes: Characterisation, Treatment and Environmental Impact: [2.1]: Early Historical Observations on Sulfide Oxidation and Acid Mine Drainage, [2.7]: Acid generation prediction*. Springer, 3rd edition.
- Maldonado, B.E., 2006. Preindustry copper production at the Archaeological Zone of the Itzapatatzo, a Tarascan location, in Michoacan. *Pennsylvania State University, Mexico*.
- Manasse, A., Mellini, M., Viti, C., 2001. The copper slags of the Capattoli Valley Campiglia Marittima. *Italy. Eur. J. Mineral.* 13, 949–960.
- Manasse, A., Mellini, M., 2002. Chemical and textural characterisation of medieval slags from the Massa Marittima smelting sites (Tuscany, Italy). *J. Cult. Herit.* 3, 187–198.
- Marghussian, V.K., Maghsoudipour, A., 1999. Fabrication of unglazed floor tiles containing Iranian copper slags. *Ceramics Int.* 25, 617–622.
- Mateus, A., Pinto, A., Alves, L.C., Matos, J.X., Figueiras, J., Neng, N.R., 2011. Roman and modern slag at S. Domingos mine (IPB, Portugal): compositional features and implications for their long-term stability and potential reuse. *Int. J. Environ. Waste Manag.* 8, 133–159.
- Meshram, P., Bhagat, L., Prakash, U., Pandey, B.D., Abhilash, 2017. Organic acid leaching of base metals from copper granulated slag and evaluation of mechanism. *Can. Metall. Q.* 56 (2), 168–178.
- Mithun, B.M., Narasimhan, M.C., 2016. Performance of alkali activated slag concrete mixes incorporating copper slag as fine aggregate. *J. Cleaner Prod.* 112 (1), 837–844.
- Mobasher, B., Devaguptapu, R., Arino, A.M., 1996. Effect of copper slag on the hydration of blended cementitious mixtures. In: Chong, K. (Ed.), *Proceedings the ASCE materials engineering conference; materials for the new millennium*, pp. 1677–1686.
- Moura, W., Masuero, A., Molin, D., Dal Vilela, A., 1999. Concrete performance with admixtures of electrical steel slag and copper slag concerning mechanical properties. *Am. Concr. Inst.* 186, 81–100.
- Moura, W.A., Goncalves, J.P., Lima, M.B.L., 2007. Copper slag waste as a supplementary cementing material to concrete. *J. Mater. Sci.* 42, 2226–2230.
- Muravyov, M.I., Fomchenko, N.V., Usoltsev, A.V., Vasilyev, E.A., Kondratova, T.F., 2012. Leaching of copper and zinc from copper converter slag flotation tailings using H₂SO₄ and biologically generated Fe₂(SO₄)₃. *Hydrometallurgy* 119–120, 40–46.
- Mututubanya, A., 2013. Cobalt recovery from old Nkana Copper Slag via solid state carbothermic reduction and sulphation, in *Metallurgy*. University of Zambia, Lusaka.
- Nadirov, R.K., Syzdykova, L.I., Zhussupova, A.K., Usserbaev, M.T., 2013. Recovery of value metals from copper smelter slag by ammonium chloride treatment. *Int. J. Mineral Process.* 124, 145–149.
- Nadirov, R.K., Syzdykova, L., Zhussupova, A., 2017. Copper smelter slag treatment by ammonia solution: Leaching process optimisation. *J. Cent. South Univ.* 24, 2799–2804.
- Nadirov, R.K., Mussapyrova, L.A., 2019. Copper Smelter Slag Leaching by using H₂SO₄ in the presence of Dichromate. *J. Chem. Technol. Metall.* 54 (3), 657–662.
- Najimi, M., Sobhani, J., Pourkhorshidi, A.R., 2011. Durability of copper slag contained concrete exposed to sulfate attack. *Constr. Build. Mater.* 25 (4), 1895–1905.
- Nikoloski, A., 2020. Paving the way for sustainable resources. *Murdoch University news article*: <https://www.murdoch.edu.au/news/articles/paving-the-way-for-sustainable-resources>.
- Osborn, G.A., Garner, F.A., Veasey, T.J., 1990. Pilot-plant study for recovery of copper metal from secondary copper slag by froth flotation. Paper presented at the *Recycling of Metalliferous Materials Conference*.
- Parsons, M.B., Bird, D.K., Einaudi, M.T., Alpers, C.N., 2001. Geochemical and mineralogical controls on trace element release from the Penn Mine base metal slag dump. *California. Appl. Geochem.* 16 (14), 1567–1593.
- Piatak, N.M., Seal, R.R., Hammarstrom, J.M., 2004. Mineralogical and geochemical controls on the release of trace elements from slag produced by base- and precious-metal smelting at abandoned mine sites. *Appl. Geochem.* 19, 1039–1064.
- Piatak, N.M., Parsons, M.B., Seal, R.R., 2014. Characteristics and environmental aspects of slags: a review. *Appl. Geochem.* 57, 236–266.
- Potysz, A., Hullebusch, E.D.V., Kierczak, J., Grybos, M., Lens, P.N.L., Guibaud, G., 2015. Copper Metallurgical Slags – Current Knowledge and Fate: A Review. *Crit. Rev. Environ. Sci. Technol.* 45 (22), 2424–2488.
- Potysz, A., Kierczak, J., Fuchs, Y., Grybos, M., Guibaud, G., Lens, P.N.L., van Hullebusch, E.D., 2016. Characterisation and pH-dependent leaching behaviour of historical and modern copper slags. *J. Geochem. Explor.* 160, 1–15.
- Potysz, A., Grybos, M., Kierczak, J., Guibaud, G., Fondaneche, P., Lens, P.N.L., van Hullebusch, E.D., 2017. Soil organic acids mobilise metals from metallurgical wastes. *Chemosphere* 178, 197–211.
- Potysz, A., Kierczak, J., Pietranik, A., Kadziolka, K., 2018. Mineralogical, geochemical, and leaching study of historical Cu-slugs issued from processing of the Zechstein formation (Old Copper Basin, southwestern Poland). *Appl. Geochem.* 98, 22–35.
- Prasad, P.S., Ramana, G.V., 2016. Imperial smelting furnace (Zinc) Slag as a structural fill in reinforced soil structures. *Geotext. Geomembr.* 44 (3), 406–428.
- Ueno, A., Kokubu K., and Uji K., 2005. A fundamental study on bleeding control of concrete containing slag fine aggregate. In: *Proceedings of 3rd International Conference on Construction Materials (Mindness Symposium): Performance, Innovations and Structural Implications*, Vancouver, Canada, 10 pp.
- Raposeiras, A.C., Vargas-Cerón, A., Movilla-Quesada, D., Castro-Fresno, D., 2016. Effect of copper slag addition on mechanical behavior of asphalt mixes containing reclaimed asphalt pavement. *Constr. Build. Mater.* 119, 268–276.
- Ravindra, K., OBE, D., Brito J.D., Mangabhai, R., Lye, C.Q., 2017. *Sustainable Construction Materials: Copper Slag*. Elsevier. pp 28–86.
- Roy, S., Datta, A., Rehani, S., 2015. Flotation of copper sulphide from copper smelter slag using multiple collectors and their mixtures. *Int. J. Miner. Process.* 143, 43–49.
- Rudnik, E., Burzynska, L., Gumowska, W., 2009. Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag. *Minerals Eng.* 22 (1), 88–95.
- Sanchez, R.M.I., Rivera, J., Frias, M., Esteban, J.L., Olaya, M., 2004. Leaching characteristics of blended mortars containing copper slag. *ACI Spl. Publ.* 221–56, 925–940.
- Sáez, R., Nocete, F., Nieto, J.M., Capitán, M.A., Rovira, S., 2003. The extractive metallurgy of copper from Cabezo Juré. *Huelva. Spain: Chemical and mineralogical study of slags dated to the third millennium b.c.* *Can. Mineral.* 41, 627–638.
- Sarrafi, A., Rahmati, B., Hassani, H.R., Shirazi, H.H., 2004. Recovery of copper from reverberatory furnace slag by flotation. *Miner. Eng.* 3 (2004), 457–459.
- Sarfo, P., Das, A., Wyss, G., Young, C., 2017. Recovery of metal values from copper slag and reuse of residual secondary slag. *Waste Manag.* 70, 272–281.
- Shamsi, M., Noparast, M., Shafaie, S.Z., Gharabaghi M., Aslani, S., 2015. Effect of grinding time on flotation recovery of copper smelting slags in Bardaskan district. *Journal of Mining & Environment*, Vol.6, No.2, 2015, 237–249.
- Sharma, R., Khan, R.A., 2017. Sustainable Use of Copper Slag in Self Compacting Concrete Containing Supplementary Cementitious Materials. *J. Cleaner Prod.* <https://doi.org/10.1016/j.jclepro.2017.03.031>.
- Shen, H., Forsberg, E., 2003. An overview of recovery of metals from slags. *Waste Manage.* 23 (10), 933–949.
- Shi, C., Meyer, C., Behnood, A., 2008. Utilisation of copper slag in cement and concrete – a review. *Resour. Conserv. Recycl.* 52, 1115–1120.
- Singh, J., Singh, S.P., 2019. Development of Alkali-activated Cementitious Material using Copper Slag. *Constr. Build. Mater.* 211 (2019), 73–79.
- Sukla, L.B., Panda, S.C., Jena, P.K., 1986. Recovery of cobalt, nickel and copper from converter slag through roasting with ammonium sulphate and sulphuric acid. *Hydrometallurgy* 16 (2), 153–165.
- Subrata, R., Amlan, D., Sandeep, R., 2015. Flotation of copper sulphide from copper smelter slag using multiple collectors and their mixtures. *Int. J. Miner. Process.* 143, 43–49.
- Tixier, R., Devaguptapu, R., Mobasher, B., 1997. The effect of copper slag on the hydration and mechanical properties of cementitious mixtures. *Cem. Concr. Res* 27 (10), 1569–1580.
- Tshiongo, N., Mbaya, R.K.K., Mawela, K., Tshabalala, L.C., 2010. Effect of Cooling Rate on base Metals Recovery From Copper Matte Smelting Slags. *World Academy Science. Eng. Technol.* 4, 236–240.
- Tümen, F., Bailey, N., 1990. Recovery of metal values from copper smelter slags by roasting with pyrite. *Hydrometallurgy* 317–328.
- Turan, M.D., Sari, Z.A., Miller, J.D., 2017. Leaching of blended copper slag in microwave oven. *Trans. Nonferrous Met. Soc. China* 27, 1404–1410.
- Urosevic, D.M., Dimitrijevic, M.D., Jankovic, Z.D., Antic, V.A., 2015. Recovery of copper from copper slag and copper slag flotation tailings by oxidative leaching. *Physicochem. Prob. Mineral Process.* 51, 73–82.
- Vestola, E.A., Kuusenaaho, M.K., Närhi, H.M., Tuovinen, O.H., Puhakka, J.A., Plumb, J.J., Kaksonen, A.H., 2010. *Hydrometallurgy* 103, 74.
- Vítková, M., Ettler, V., Johan, Z., Kribek, B., Sebek, O., Mihaljevic, M., 2010. Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province. *Zambia. Mineral. Mag.* 74 (4), 581–600.
- Wang, X., Geysen, D., Padilla, S.V., D'Hoker, N., Van Gerven, T., Blanpain, B., 2013. Characterization of Copper Slag. *The Minerals, Metals & Materials. Society*.
- Wu, W., Zhang, W., Ma, G., 2010a. Optimum content of copper slag as a fine aggregate in high strength concrete. *Mater. Des.* 31 (6), 2878–2883.
- Wu, W., Zhang, W., Ma, G., 2010b. Mechanical properties of copper slag reinforced concrete under dynamic compression. *Constr. Build. Mater.* 24 (6), 910–917.

- Yang, Z., Rui-lin, M., Wang-dong, N., Hui, W., 2010. Selective leaching of base metals from copper smelter slag. *Hydrometallurgy* 103, 25–29.
- Yucel, O., Addemir, O., Tekin, A., & S. Nizamoglu., 1992. Recovery of Cobalt from Copper Slags, *Mineral Processing and Extractive Metallurgy Review: An International Journal*, 10:1, 99-107, DOI: 10.1080/08827509208914078.
- Yuksel, U., Tegin, I., 2017. Recovery of Copper and Cobalt from Copper Slags as Selective. *J. Environ. Eng. Sci.* 6, 388–394.
- Zain, M.F., Islam, M.N., Radin, S.S., Yap, S.G., 2004. Cement-based solidification for the safe disposal of blasted copper slag. *Cem. Concr. Res.* 26 (7), 845–851.
- Ziyadanogullari, R., 1992. A new method for recovering Fe(II) sulphate, copper, and cobalt from converter slag. *Sep. Sci. Technol.* 27, 389–398.