

## Article

# Feasibility of Recovering Valuable and Toxic Metals from Copper Slag Using Iron-Containing Additives

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**Abstract:** One of the greatest environmental challenges in metal extraction is the generation of a large amount of slag. Most of these slags contain insufficient amounts of valuable metals for economical revalorization, but these concentrations may be harmful for the environment. At present, more than 80% of the global copper products are obtained by the smelting process, where the major by-products are various slags containing a broad range of almost all known elements. In this study, valuable and potentially harmful elements were recovered from mining waste using gravity separation and gravity settling. The settling process was enhanced by injecting coke, ferroc carbon, ferrosilicon, and ferrosulfide. In total, 35 elements were detected in the samples using electron probe microanalysis. After the treatment, 89.4% of the valuable, toxic, and trace elements gathered in the newly formed matte after maintaining the copper slag for four hours at 1300 °C and adding ferrosilicon. The metallic constituents of slags could be an important source of raw materials and they could be considered an environmentally beneficial source of copper and other materials. Suggested practices can prevent harmful elements from entering the environment, generate value from the gathered metals, and make the remaining slag suitable for construction or mine backfill materials. The present article also assesses the challenges in slag processing by the pyrometallurgical route and provides a roadmap for further investigations and large-scale studies.



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**Keywords:** mining waste; settling; recovery; heavy metals; slag; additives

## 1. Introduction

Along with iron and aluminum, copper is the most commonly used metal by humans, with global mine extraction estimated at 22 million metric tons in 2022 [1]. At present, more than 80% of the global copper products are obtained by the smelting process [2], where the major by-products are various slags containing a broad range of almost all known elements [3]. The production of one metric ton of copper generates between two and three tons of copper slag [4]. Accordingly, in 2022, at least 45 million tons of slag were added to the already accumulated slag from the previous several centuries of copper extraction [5]. Although the disposal of copper slag is considered the least favorable option, this trend will continue even at a higher rate [6,7].

Since 1902, 652 Mt of ore has been extracted from the Bor region, yielding 4.93 Mt of copper and 280 metric tons of gold. Currently, slagheaps, mine tailings, and open pits dominate the landscape, as shown in Figure 1. Known mineral resources of the Bor metallogenic zone are estimated to be over 20 Mt of copper and 1000 t of gold [8]. Recently, massive sulfide mineral deposits were found, containing more than 10 Mt of ore with 5.6% copper and 2.6 g/t gold [9], having the highest rank on the world's deposit scale [10], while the nearby deposit is estimated to contain 45 Mt of ore with 3% copper. As mining in

the Bor region continues, new methods to prevent the disposal of harmful materials and reclaim valuable metals should be considered [11].



**Figure 1.** Bor basin in Serbia contains large slagheaps and mine tailings in proximity to densely populated areas.

Various remediation methods for mining waste have the potential to mitigate the challenges associated with slag disposal [12,13]. Recently, to maximize the utilization value of copper slag according to the environmental impact and decarbonization, the reduction of copper slag with hydrogen was proposed by Zhang et al. [14], studying the kinetics of this process. Suitable conditions for reduction were a temperature of 1100 °C, a hydrogen partial pressure of 40%, and a calcium oxide addition amount of 30%. Under these conditions, the metal reduction ratio was 85.12%. The activation energy of the hydrogen reduction copper slag was 29.107~36.082 kJ/mol, which decreased gradually with an increase in the hydrogen partial pressure. Similar results may be achieved by using additives, which may ease the settling processes of the metals or induce chemical reactions that can extract valuable metals from sulfide or oxide compounds.

An ideal additive should have a melting point below the temperature required in the extraction process and the overall chemical reaction of assimilation should be exothermic, which will significantly ease the maintenance of the operating temperature inside the converter [15]. The density of the additive should be higher than that of the slag because it would cause its slow descent towards the bottom of the converter through the liquid slag, thus providing the highest mixing and contact area between the additive surface and the liquid slag. The exothermic chemical reaction between the additive and the slag further improves the assimilation efficiency and decreases the dependence on fossil fuels or electricity to maintain the operating temperature inside the converter [16]. The major components of copper slags are FeO and SiO<sub>2</sub>, with a chemical composition close to Fayalite (52 wt%, Fe–10.8 wt%, and Si–29 wt% O) and a melting temperature close to its congruent point of 1205 °C. Overall, in an industrial environment, considering the trade-off between cost, affordability, efficiency, and environmental impact, iron-containing additives show the best results.

In this study, gravity separation and gravity settling of metals were employed to recover most metals from slag, which is a by-product of the copper extraction process and is disposed of near densely populated areas. The slag samples were crushed into particles smaller than 2000 µm, separated from low-density particles that did not contain heavy metals, and heated at high temperatures for four hours to induce the coalescence of dense elements. Low-density particles separated by heavy media separation and slag remaining formed by high-temperature treatment are inert and not detrimental to the surroundings, whereas the added value of the recovered metals may reduce the processing costs of the implemented procedures.

## 2. Kinetic Parameters for Recovery of Valuable Metals at High Temperatures

Although the extraction methods are similar, higher concentrations of valuable metals are found in slags formed during the pyrometallurgical extraction of nickel and cobalt than in slags formed during the extraction of copper. Professor Utigard's group at the University of Toronto conducted comprehensive research on kinetic parameters during the recovery of valuable metals to understand the influence of time, temperature, and flux addition on Cu, Ni, and Co recovery from nickel/cobalt slags [17,18]. Temperatures slightly different from those used in the conventional extraction process do not significantly affect the energy balance. During the additional slag treatment process, the highest gains in valuable metal recovery were achieved by injecting carbonless reducing agents, although widely available industrial additives also achieved significant recoveries [19,20]. Regarding the settling process in nickel/cobalt slag, Mitrašinović and Wolf [21] found that the most favorable temperature was 1300 °C, for one hour of settling time, considering the ratio between the value of the extracted metals and the energy invested in maintaining the slag in the liquid state, while, when settling for longer than four hours, no significant gains in metal recovery were recorded.

## 3. Materials and Methods

Slag samples were extracted from the Bor slagheap location adjacent to the downtown area of the city and west of the Old-Bor tailing pit. Typical samples from a particular site contain approximately three percent sulfide minerals and 0.2% metallic copper.

The collected samples were crushed into particles less than 2000 µm in size and separated using a solution of lithium metatungstate ( $\text{Li}_6(\text{H}_2\text{W}_{12}\text{O}_{40})$ ) as a heavy liquid media (HLM) separator with a density adjusted to 2.85 g/cm<sup>3</sup> and viscosity of 10 cP. By HLM separation, soil residues and pure SiO<sub>2</sub> with a density of 2.65 g/cm<sup>3</sup> were separated from the slag where most of the metals were located [22].

Crushed particles of the copper slag rich in dissolved or embedded metals produced by HLM separation were placed into a cylindrical alumina crucible measuring 17 cm in height and 3.8 cm in inner diameter and flushed with argon gas to prevent the uncontrolled oxidation of oxygen from the air (Figure 2). After the liquefied slag reached 1300 °C, milled iron-containing additives were distributed along the surface of the molten slag and left to assimilate. After the assimilation of the additives, limestone was added as a flux to the top of the liquid slag. The total weight of the examined sample was 425 g, which consisted of 400 g of copper slag, 20 g of additive, and 5 g of flux. The duration of treatment at a high temperature was set at four hours, after which the treated slag samples were allowed to cool to room temperature. The cooled samples were detached from the alumina crucible, while the matte and remaining slag were separated at the interface, as shown in Figure 3. Gravimetric, metallography, and chemical analyses were performed on both the matte and remaining slag.

The mineralogical composition of the initial slag was determined using a PW 1830/40 X-ray Diffractometer (Philips, Almelo, Netherlands) at a voltage supply of 40 kV, with a current intensity of 20 mA, from a 10- to 90-degree 2θ angle with a 0.1-degree measurement step. Concentrations of valuable, toxic, and trace elements were detected in the slag samples using an electron probe micro-analyzer (EPMA) consisting of a S-570 scanning electron microscope (Hitachi Ltd., Tokyo, Japan) with a Cameca SX50 microprobe capable of detecting elements from <sup>5</sup>Boron to <sup>92</sup>Uranium. Iron, as a bulk element, was analyzed using the titrimetric method at IPL International Plasma Labs, Ltd., in Vancouver, Canada.

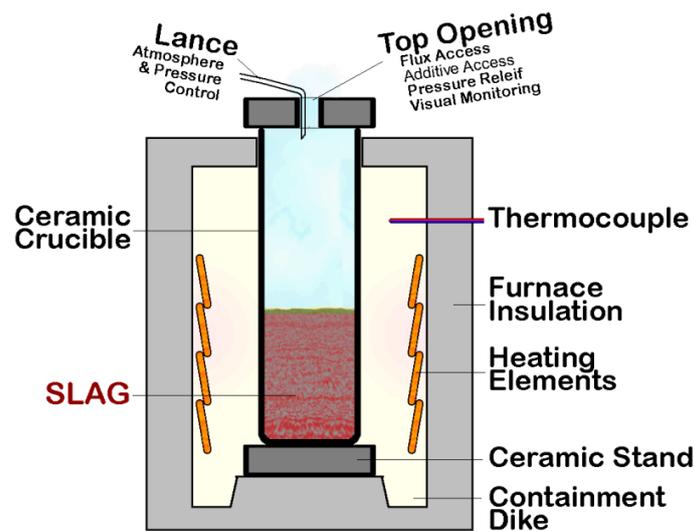


Figure 2. Gravity settling of the valuable and toxic metals at the bottom of the crucible.

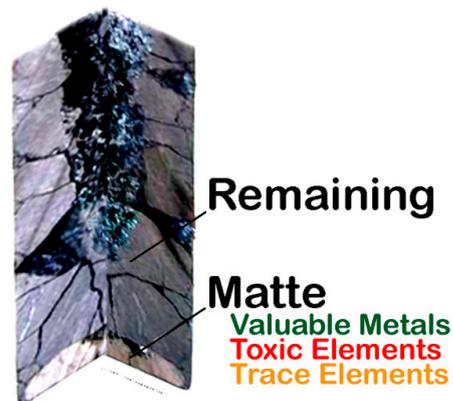


Figure 3. Macrostructure of the sample before separation, revealing the interface between the matte and the remaining slag. The specimen diameter is 3.8 cm.

## 4. Results

Because the examined slag was disposed of in a landfill for many years, the main purpose of the gravity separation was to separate the soil components and other residue materials from the slag. In all instances, the lighter fraction was less than 10 wt% of the mining waste mass, leaving only the slag particles at the bottom of the separation vessel.

### 4.1. Mineralogical Characteristics

X-ray diffraction analysis of the copper slag samples obtained from the Bor copper slag landfill showed that the dominant mineralogical components were fayalite and magnetite (Figure 4). These slags contain significant quantities of dissolved metals or metallic particles embedded in the fayalite matrix (Figure 5a). The most common ore minerals that remained in the slag sample were sulfidic solid solutions of copper and iron such as  $\text{Cu}_5\text{FeS}_4$ ,  $\text{Cu}_2\text{S}$ , and  $\text{Cu}_9\text{S}_5$  (Figure 5b). The metallic constituents of slags could be an important source of raw materials and they could be considered an environmentally beneficial source of copper and other materials [23,24].

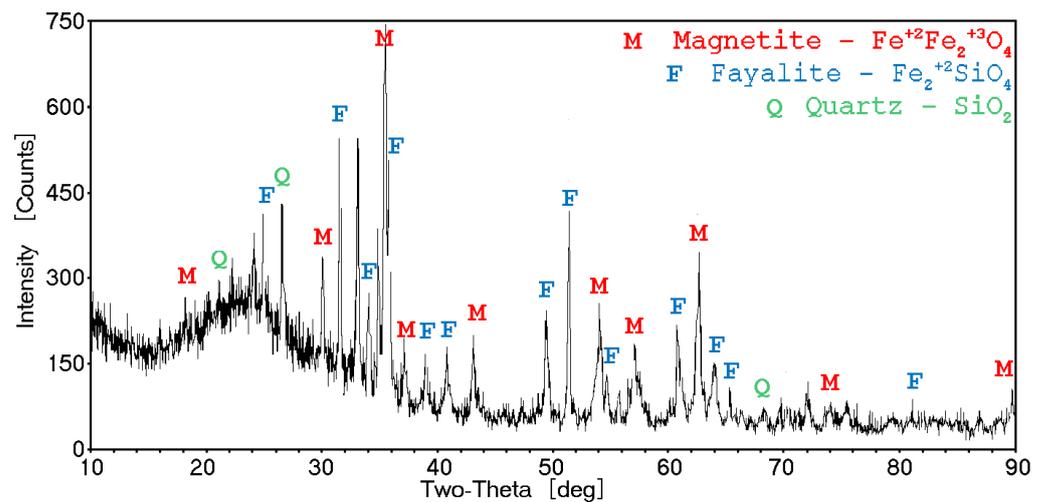


Figure 4. X-ray diffraction analysis of the bulk slag sample.

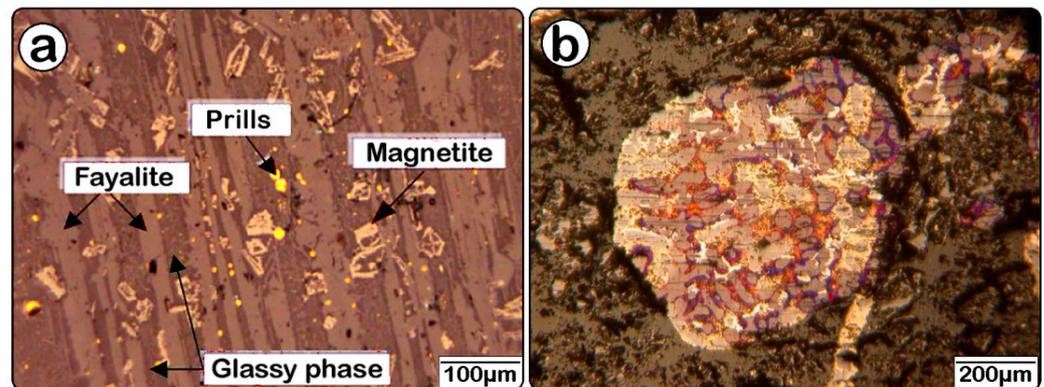


Figure 5. (a) Micrograph of copper slag [25] and (b) a large metallic prill embroiled inside the slag.

#### 4.2. Chemical Composition

Based on the concentrations obtained by the electron probe micro-analyzer, elements are grouped concerning their quantities, reusability, and toxicity. Oxidic metals can also be used as construction materials. Valuable metals are present in sufficient quantities and can be further extracted and placed on the market. Heavy and toxic metals are present in quantities that cannot generate a profit in the market, but such quantities may harm the environment, while trace elements are present in low concentrations that can neither provide precise quantitative analyses nor have detrimental effects on the environment. The elemental concentration of the initial slag (initial slag) is given, together with mattes chemical compositions (matte: no additive, coke, FeC, FeSi, and FeS), in Table 1.

Most slag elements are bound as oxides, sulfides, or complex minerals, with iron, silicon, oxygen, and sulfur constituting 95% of the mass. Table 1 lists the concentrations of 35 elements detected in the slag samples. Non-detected elements may be present in trace amounts and therefore are omitted from further analyses. The electron probe microanalysis revealed the chemical compositions of valuable, toxic, and trace elements. Comparing the outcomes of two techniques, titrimetric and electron probe microanalysis analyses, the differences in the iron concentrations in the initial slag and mattes generated after metal gravity settling were in the range of zero to 0.28%, as given in Table 2.

**Table 1.** Normalized assay of copper slag and generated mattes after metal gravity settling for four hours at 1300 °C with various additives.

Element		Initial Slag, wt%	No Additive	Coke	Matte, wt%			Detection Limit, wt%	Sensitivity, wt%
					FeC	FeSi	FeS		
Oxidic	Fe *	49.85	33.45	35.35	43.30	43.65	34.40	0.01	0.01
	Si	11.12	3.10	2.90	2.95	3.80	3.15	0.05	0.01
	Ca	0.15	nd	nd	nd	nd	nd	0.1	0.05
Marketable	Al	2.77	4.69	4.42	4.61	3.77	2.72	0.01	0.01
	Cu	0.97	16.45	25.57	20.44	18.40	18.46	0.01	0.01
	Cr	0.71	8.03	7.90	8.35	8.41	7.65	0.01	0.01
	Mg	0.06	0.29	0.28	0.3	0.31	0.27	0.02	0.01
	Mn	0.02	0.13	0.13	0.13	0.13	0.12	0.01	0.01
	Ni	0.031	0.23	0.23	0.24	0.25	0.22	0.005	0.001
Toxic	As	0.038	0.009	0.009	0.008	0.007	0.009	0.001	0.001
	Cd	0.057	0.533	0.527	0.558	0.581	0.515	0.0005	0.0005
	Hg	0.079	1.659	1.934	2.023	1.930	1.783	0.0005	0.0001
	Mo	0.02	0.21	0.21	0.215	0.215	0.185	0.0005	0.0005
	Pb	0.07	1.390	1.490	1.670	1.640	1.450	0.001	0.0005
	Sb	0.02	0.105	0.105	0.110	0.110	0.105	0.001	0.001
	Se	0.17	1.26	1.24	1.31	1.31	1.21	0.01	0.01
	Te	0.23	2.74	2.695	2.845	2.96	2.93	0.01	0.005
Zn	0.037	0.012	0.012	0.012	0.010	0.011	0.001	0.001	
Trace	Ba	0.007	0.090	0.095	0.105	0.115	0.090	0.0005	0.0005
	Co	0.01	0.10	0.10	0.11	0.12	0.09	0.001	0.001
	Sr	0.01	0.129	0.127	0.135	0.135	0.122	0.001	0.0005
	Ti	0.005	0.005	nd	nd	nd	nd	0.005	0.005
Not Detected	B	nd **	- ***	-	-	-	-	0.05	0.05
	Bi	nd	-	-	-	-	-	0.005	0.005
	K	nd	-	-	-	-	-	0.1	0.1
	Na	nd	-	-	-	-	-	0.05	0.05
	La	nd	-	-	-	-	-	0.005	0.005
	P	nd	-	-	-	-	-	0.01	0.01
	Sc	nd	-	-	-	-	-	0.01	0.005
	Tl	nd	-	-	-	-	-	0.01	0.005
	V	nd	-	-	-	-	-	0.005	0.005
	W	nd	-	-	-	-	-	0.001	0.001
Zr	nd	-	-	-	-	-	0.005	0.005	
Other Nonmetals	S	1.67	21.49	12.84	9.94	11.92	21.57	0.01	0.01
	O	31.9	3.91	1.84	0.66	0.22	2.96	0.01	0.05
Summation		100.0	100.0	100.0	100.0	100.0	100.0		

Note: \* iron was analyzed by titrimetric analysis; \*\* nd denotes non-detected; \*\*\* dash (-) denotes not measured.

**Table 2.** Comparison of iron concentrations obtained by titrimetric and EPMA analyses, in wt%.

Analysis Type	Initial Slag	No Additive	Coke	Matte FeC	FeSi	FeS	Detection Limit	Sensitivity
Titrimetric	49.85	33.45	35.35	43.30	43.65	34.40	0.01	0.01
EPMA	49.75	33.40	35.25	43.20	43.65	34.35	0.05	0.01
Difference, %	0.20	0.15	0.28	0.23	0	0.14		

#### 4.3. Recoveries

In the investigated slag from the Bor municipality, valuable metals represented 4.56 wt%, with 0.72 wt% heavy and toxic metals, while the rest were oxidic metals. The total matte recovered or yield ( $\Gamma_{Matte}$ ) after high-temperature treatment can be assessed utilizing a mass balance by applying the following equation:

$$\Gamma_{Matte} = \frac{m_{Matte}}{m_{Total}} * 100, \text{wt\%} \quad (1)$$

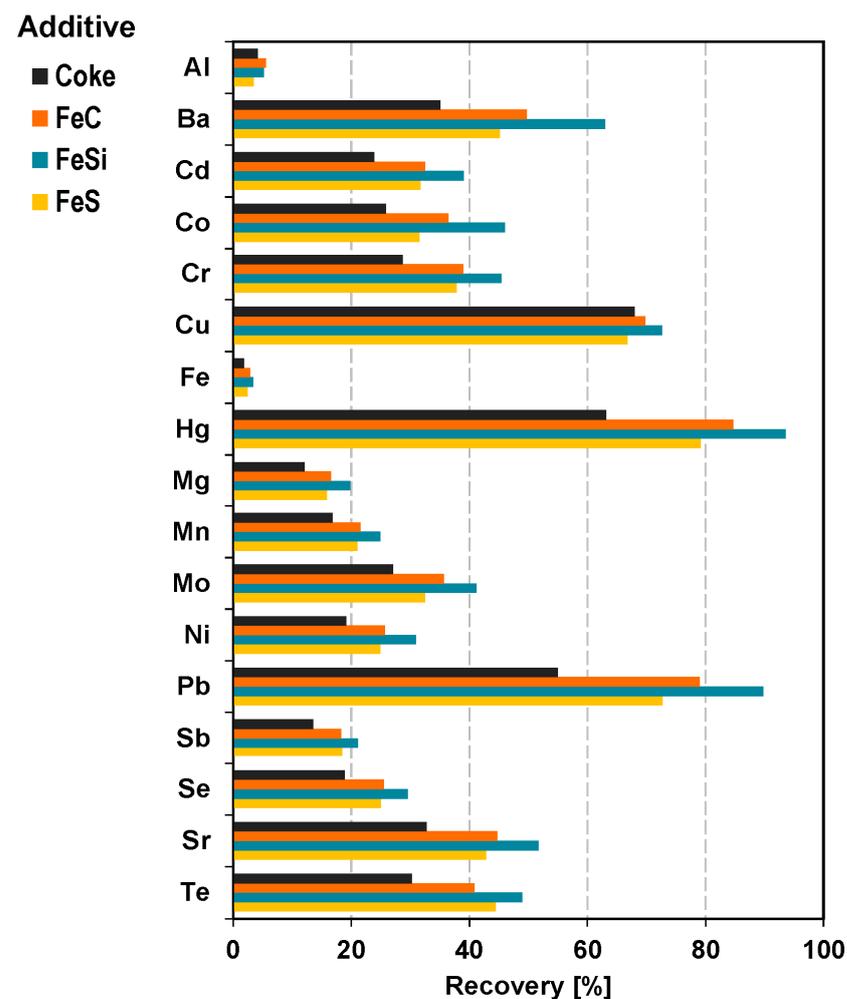
where  $m_{Matte}$  is the weight of the matte recovered, while  $m_{Total}$  is the weight of the initial mixture of the slag, additive, and flux. The recovery and partition coefficients of elements can be calculated by comparison of the particular element concentration in the matte versus the concentration of the particular element in the bulk slag the following equation:

$$\zeta_{Recovery} = \frac{\Gamma_{Matte} * C_{Matte}^{\zeta}}{C_{Slag}^{\zeta}}, \text{wt\%} \quad (2)$$

where  $\zeta_{Recovery}$  is the value of the particular element recovered in the matte, while  $C^{\zeta}$  is the elemental concentration in the respective phases. The matte quantities are given in Table 3. Since the metal coalescence and the formation of a matte are based on elemental diffusion, sufficient time and temperature should be provided [26]. However, gravity is the main driving force for elemental diffusion, allowing elements with a higher density to sink to the bottom of the containing vessel, which otherwise would remain in the slag [27]. The recovery for each analyzed element, after high-temperature treatment, is given in Figure 6. Oxidic metals predominantly bound to the oxygen and formed the remaining slag. Elements with a low sublimation temperature [28,29], such as arsenic or zinc, were removed below the detection limits in the matte as well as in the remaining slag. All other elements were recovered proportionally to their density values in the liquid state.

**Table 3.** Matte yield from the initial 425 g sample mass by keeping slag for four hours at 1300 °C.

Additive	Yield, g	Yield, %
-	17.8	4.19
coke	11.0	2.59
ferrocarbon	14.1	3.32
ferrosilicon	16.3	3.83
ferrosulfide	14.9	3.51



**Figure 6.** Elemental recoveries after metal gravity settling.

#### 4.4. Settling with Iron-Containing Additives

In the typical pyrometallurgical industrial treatment of the ores' concentrates, approximately 95% of metals are extracted. Keeping fayalite slags at 1300 °C for four hours and slow cooling resulted in the significant coalescence, at roughly five percent, of these non-extracted metals and the formation of a matte consisting mostly of metals in elemental or sulfide form. In this work, high-temperature slag treatment resulted in a new trade-off, where 74.6 wt% of these metals were recovered without the use of additives. After adding additives to the liquidized slag, the recovery of metals increased to 89.4% when ferrosilicon was used.

The chemical composition of copper slag, shown in Table 1, indicates the slag's predominantly fayalite structure and overall significant metal recovery after high-temperature treatment (metals up, oxides down). During the high-temperature treatment, most of the oxygen was bound to the oxidic metals and stayed in the remaining slag, while the formed matte was rich in valuable and toxic metals (Figure 7). The effective separation of metals in the matte from non-metals in the remaining is noticeable (metals up, non-metals down). The addition of ferrosilicon formed a matte with the lowest oxygen and iron content, which was 30% higher than in the matte formed without using additives. The pig iron decreased the basicity [30] and resulted in a matte with the highest degree of metallization and with the lowest level of sulfur and a low level of oxygen, with similar iron content to the matte formed with ferrosilicon additive. Unlike other additives, the addition of ferrosulfide did not significantly improve the metals' coalescence process.

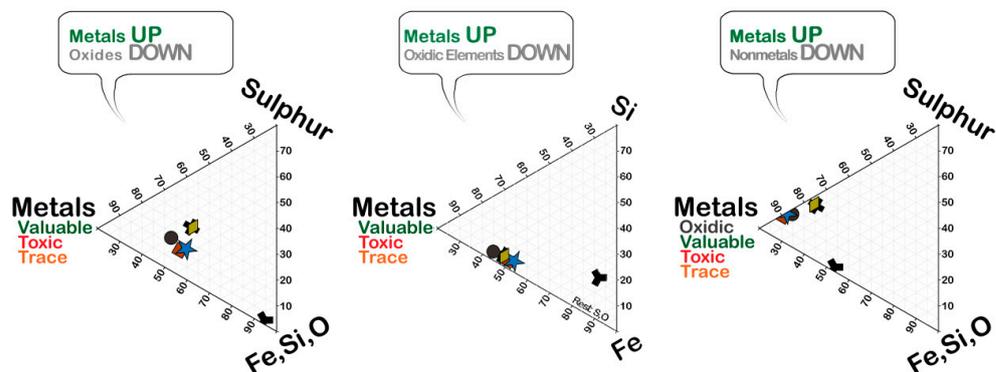
### Mining Waste

➔ Copper Slag

4h  
1300°C

### Matte

- ★ No Additive
- Coke
- ◆ FeC
- ★ FeSi
- ◆ FeS



**Figure 7.** Elemental distribution in initial slag and formed matte after the treatment, indicating the effect of additives and the overall effectiveness of the recovery method. Axis values are in wt%.

All the remaining slag depleted in valuable metals fell within the narrow range of 20 to 30 wt% SiO<sub>2</sub>. This composition range corresponds to the 2FeO:SiO<sub>2</sub> phase, which explains why fayalite was seen as the major constituent in the initial slag and all remaining. The addition of reducing agents increased the ratio between SiO<sub>2</sub> and FeO in the remaining, which was an additional benefit since some iron was recovered together with other metals.

## 5. Discussion

Carbon-based additives are extensively used in non-ferrous metal extraction practices because of their availability and market price. The primary additives for the chemical reduction of metal-containing concentrates are coke, coal, pig iron, ferrosilicon, and ferrosulfide, while CaO and SiO<sub>2</sub> are often used as fluxes. The same, widely available, additives may be used in an attempt to recover valuable and harmful elements from slags. Ideal additives should have a low melting temperature, slightly higher density than the slag, and the potential to facilitate exothermic reactions without producing gaseous products such as CO<sub>x</sub> or SO<sub>x</sub>. Coke and coal cause the formation of CO and CO<sub>2</sub> and have a high melting point, which slows down the assimilation process, but the low cost makes them the

most used additives in metal extraction processes. Contrary to carbon-containing additives, ferrosulfide has a relatively low melting point at 1194 °C and a good density of 4.84 g/cm<sup>3</sup>, with only the adverse effect of generating low amounts of SO<sub>x</sub> gases during its assimilation. Ferrosulfide's assimilation is followed by energy release, which further compensates for its relatively higher cost than coke.

Although carbon-based additives are by far the most cost-effective, metal recoveries are achieved at higher energy costs and settling times. The addition of ferrocarbon into liquid slag improves the metal recovery, but assimilation relies only on the dissolution process because of its high melting point. Ferrosilicon is another widely used reducing agent in the non-ferrous industry. The melting point of ferrosilicon is similar to that of the fayalite-based slags, but its exothermic potential improves the overall energy balance and settling time. The injection of ferrosilicon immediately allows chemical reactions, where the released energy is sufficient to melt the rest of the additive. The density of the ferrosilicon additive, similar to ferrosulfide, is slightly higher than the density of the liquid bath [31].

### 5.1. Process Optimization

In a slag kept above the liquidus temperature, two concurring phenomena contribute to coalescence and subsequent metal separation from the bulk material, namely the chemical reduction of dissolved metals and the settling of these metals at the bottom of the containing vessel. The aim is to provide conditions for effective additive assimilation with the lowest energy investment. The use of additives enhances the process by reducing metallic oxides into either elemental or sulfide forms, while at the same time reducing solid magnetite to liquid FeO, which decreases the slag's viscosity and improves the recovery rate [32,33]. Major elements in the fayalite slags formed after copper extraction processes are iron, silicon, and oxygen. The pseudo-binary phase diagram of the FeO and SiO<sub>2</sub> system is given in Figure 8, emphasizing the area around the congruent point at 1205 °C. At the congruent point, the ratio between FeO and SiO<sub>2</sub> is two to one and corresponds to the concentrations of 54.81 wt% Fe, 13.78% Si, and 31.41 wt% oxygen. Although higher temperatures favor metals' coalescence, in a practical sense, adjusting the chemical composition around congruent points provides the minimal operational temperature and consequently the lowest cost for the applied process [34].

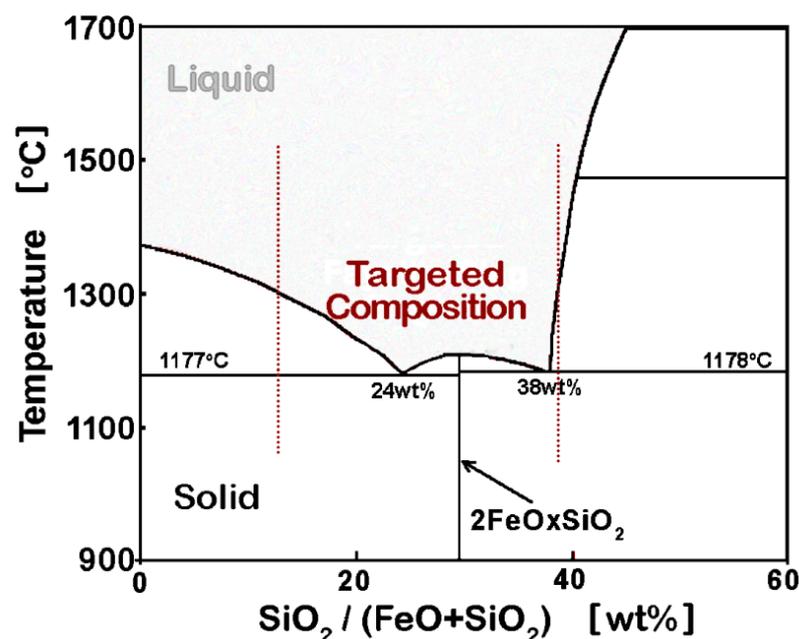


Figure 8. Pseudo-binary phase diagram of the FeO and SiO<sub>2</sub> system calculated by FactSage software using data from the SGTE2007 database [35].

While the emphasis in this work was on the effect of additives on the improvement of extraction procedures, extending the focus to a large-scale operation would include the influence of the inhomogeneity in temperature, composition, density, viscosity, and other factors that affect the elemental mass flow in large vessels.

### *5.2. Challenges in Obtaining Comparable Chemical Composition of the Slag*

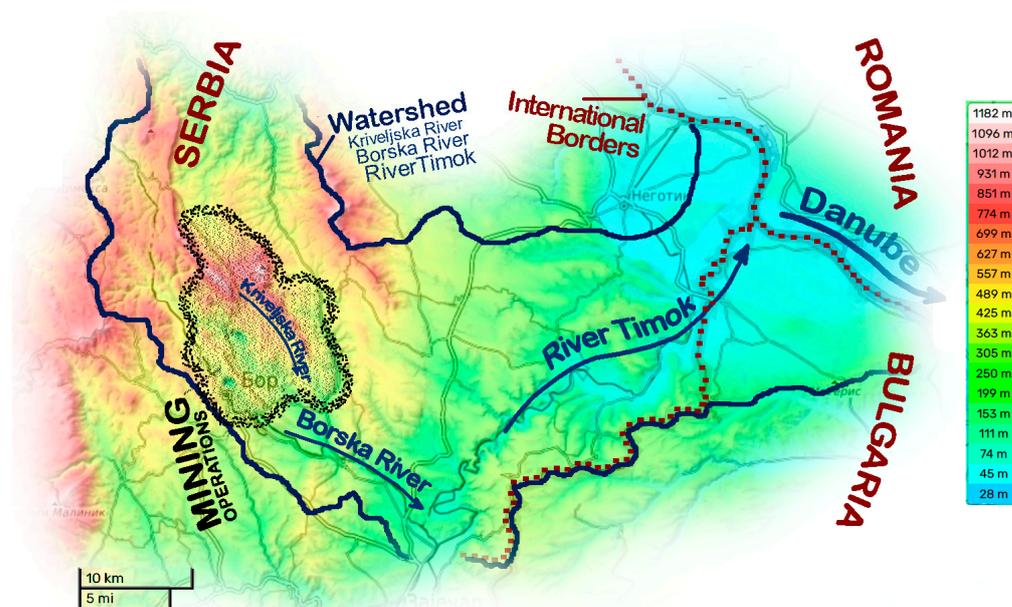
Slags are some of the most complex materials regarding either the number of containing elements or the microstructural constitution. The presence of almost all elements seen in the periodic table (found in elemental form as well as parts of complex minerals, oxides, sulfides, or carbides), in quantities from trace elements to bulk, makes accurate chemical analysis one of the most challenging steps in the mineralogical research endeavor. Electron probe microanalysis (EPMA) is becoming the most convenient method for elemental analysis, expanding its accuracy to elemental concentration ranges from trace to bulk [36]. Recent advances in energy-dispersive X-ray spectrometry (EDS) allow for simultaneous quantitative concentration data gathering regarding the minor and trace elements. With measurement differences between titrimetric and EPMA methods below 0.28% in the concentrations of bulk elements such as iron, the EPMA results could be considered quantitative as well. In complex materials containing tens of elements in bulk or trace concentrations, such as copper slags, the simultaneous analysis of all elements in the periodic table may omit the need for the normalization of compositional assays, which could further simplify the development of mathematical and general solution models [37,38].

### *5.3. Toxicity Considerations*

The increased content of toxic elements and increased acidity of the soil are typical characteristics in mining waste sites. Toxic metals primarily include those that are not biogenic, e.g., cadmium, lead, mercury, chromium, and arsenic. However, many other metals, which are considered necessary for the normal functioning of all living organisms, if they are present in excessively high concentrations, can become harmful. In this work, the concentrations of all potentially toxic elements coalesced in the matte at the bottom of the containing vessel and were collected for further valorization. For example, the concentration of copper in soil worldwide is between 190 and 310 mg/kg, while the allowed concentrations of zinc in soil are from 300 to 720 mg/kg [39].

### *5.4. Environmental Considerations*

Copper ore exploitation and processing in the Bor municipality has created large areas of disposed slag. Considering the number of valuable metal deposits in the entire Bor region, exploitation will continue for many decades [40]. The formation of large land areas with slags inevitably leads to a rise in wastewater because of the natural leaching processes of mining waste. Initial seepage waters can transform into natural springs that further disembody into the river flows [41] and affect the natural habitats of many species [42,43]. Once the mine waters reach river flows, then the containment planned at the local level may be extended to much larger areas, eventually becoming an international environmental concern (Figure 9). However, the remaining mining waste after treatment with various additives is depleted of heavy metals and has strong intermolecular bonds and therefore is very stable and impervious to atmospheric conditions. Remediation of these materials as construction or backfill materials [44,45] can prevent environmental damage and reduce the costs of the transportation and storage of potentially harmful materials [46–48].



**Figure 9.** The area affected by the mining activities. The elevation map with watersheds and basins of the Kriveljska River, Borska River, and River Timok, and their positions concerning the mining activities.

## 6. Conclusions

The amount of slag produced and landfilled near the Bor municipality is estimated at several million tons. The mineralogical composition of the slag showed that the most dominant oxide minerals were fayalite and magnetite, while the most dominant metallic minerals were solid solutions of Cu-Fe-S.

In some locations, the concentrations of valuable metals are below the limits of economical revalorization, but these concentrations may be harmful to the environment. Gravity separation followed by gravity settling procedures achieved up to 89% recovery when industrial additives were used, implying that the introduction of new reducing agents may further increase the separation and coalescence of metals that otherwise would be disposed of in landfills. The major components of the remaining slag depleted of metals after heating the slag to 1300 °C for four hours were iron and silicon oxides. Such compounds are already abundant in the Earth's crust and would not impose an environmental threat. These compounds have strong intermolecular bonds and therefore are very stable and impervious to atmospheric conditions. The suggested procedure reduced the concentrations of potentially toxic metals to levels in line with the local regulations, which made the remaining slag suitable, with further assessments, for a construction or backfill material. The newest challenge is to develop sustainable pathways to recover non-ferrous metals from slags using hydrogen as an enabler for waste immobilization and metal valorization in carbon-free processes.

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