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# Copper Removal Methods From Steel — A Critical Assessment

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## ABSTRACT

In this study, different existing methods to remove alloyed and coated copper from steel are summarized, compared, and discussed. None of these methods have been scaled up industrially so far. Characterization of industrial steel scrap will indicate in which forms and quantities copper is present. Based on environment, economics and process efficiency, the most promising techniques will be selected for further investigation. The study will then focus on ways to bring the process efficiency to the level required for industrial application, by better understanding of thermodynamic limits and the reaction kinetics. Possible removal of other undesired elements from the scrap will be taken into account as well.

Keywords: Decopperization, tramp elements, scrap, circularity, process

## INTRODUCTION

In the last 50 years, humankind has become increasingly aware of the necessity to restrict and even lower its impact on the global environment. Reducing carbon footprint to mitigate climate change and increasing circularity to become more sustainable are prime targets for the global industry, and the steel industry in particular because of its relatively large impact on the environment. Therefore, the European Union has set ambitious goals for making the European steel industry more circular and sustainable [1]. Significantly boosting the share of scrap as an input in steelmaking replacing virgin iron ore will increase steel circularity and decrease the carbon footprint of steelmaking. Copper in steel can lead to hot shortness (leading to surface cracks), decreases ductility, decreases the r-value (strain ratio), and lower the weldability. Although copper can also have a positive impact on the steel properties, like increasing hardness and corrosion resistance, most steel grades have a maximum copper concentration to limit its detrimental effects on the steel [2-4].

Since iron ore is virtually copper free, scrap is the main source of copper in steelmaking. The copper from the scrap will dissolve in the newly produced steel when scrap is used as raw material. Significantly increasing the scrap input in steelmaking leads to a higher input of copper into the steel. Furthermore, the availability of scrap with a low copper content is limited. Therefore, if steelmakers increase their scrap consumption, they will have to purchase more obsolete scrap with typically a higher copper content. This leads to an even higher increase in copper input than can be expected on the increase of total scrap input alone. On top of that, the presence of copper in steel scrap has been increasing since the 1960s and is predicted to increase further even more in the coming decades [5].

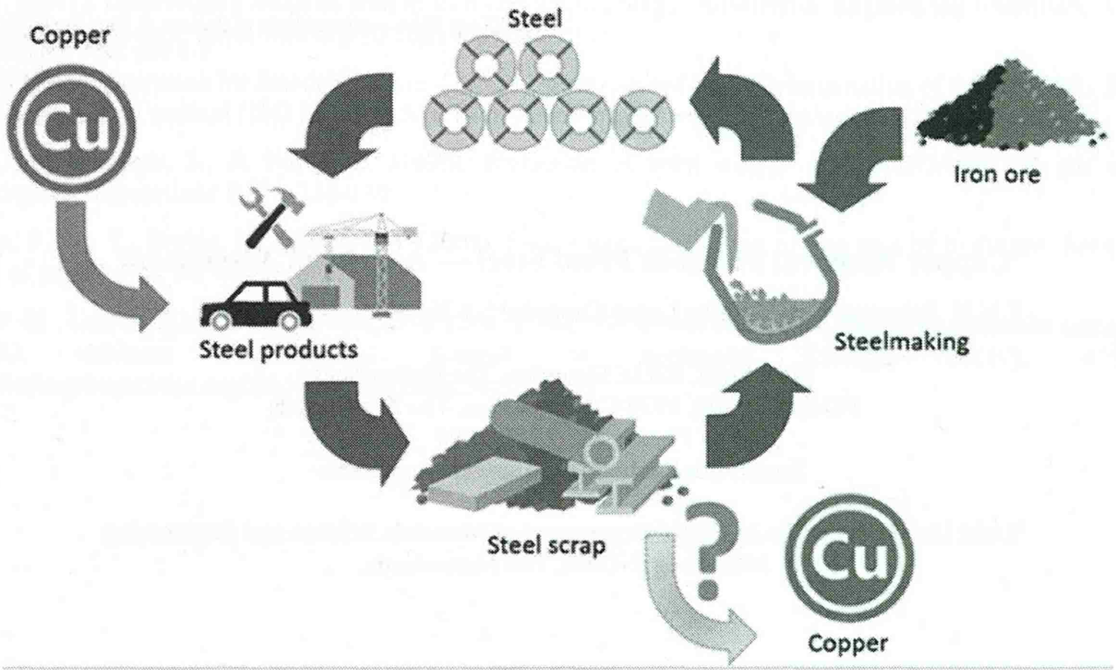

Figure 1. Life cycle of copper in steel.

Copper can be present in scrap in physically loose form (like wires or copper objects), coated on pieces of steel or alloyed in the steel scrap. Currently, loose copper can be removed by a combination of shredding, magnetic separation and density separation, or, alternatively, by detection via X-Ray Fluorescence and automated sorting/separation, or simply by hand picking. Although some loose copper can be difficult to remove, e.g. when copper wires are inside a piece of steel scrap, called a 'meatball', or it is physically bound with steel parts, extensive shredding or other pretreatment methods can result in removing over 90% of the loose copper.

For removing coated and alloyed copper, no methods are available on an industrial scale. This means that once the copper is in the steel, it stays in the steel, since there is no way to remove the copper from the steel life cycle (see Figure 1). Today, steelmakers mitigate the detrimental effects of copper in the steel from the scrap by diluting their steel with ore-based virgin iron (e.g. from BF or direct reduced iron, DRI), which is virtually copper-free. Given the demand for more circularity in steelmaking, diluting the steel with virgin material will no longer be sufficient to control the copper content of the new steel products. Instead, new strategies must be investigated to mitigate the negative effects of copper in steel. Copper removal from steel will be essential in that strategy and will slow down or even stop the build-up of copper in steel worldwide.

## THEORETICAL BACKGROUND

In steelmaking, the removal of elements dissolved in Fe typically takes place by oxidation (C, Si, P, Mn, Ti) or by a reaction with oxides in a reducing environment (S) [6]. Removing elements from iron by oxidation works for elements that have a lower free Gibbs energy of oxide formation. However, as soon as elements are above iron, or close to it (like V and even Cr), in the Ellingham diagram (see Figure 2), their oxides present a higher Gibb's free energy of formation, which means that oxidation is no longer a viable refining method since iron will have a preference to react with the oxygen available. Therefore, the Ellingham diagram can be used to predict which elements, once they are dissolved in iron, are problematic for steelmakers. Of the typical problematic unwanted elements in steel, copper is the most noble. Thus, during the oxygen blowing of the steelmaking process (BOF converter or EAF), virtually no copper will be oxidized and end up in the slag phase.

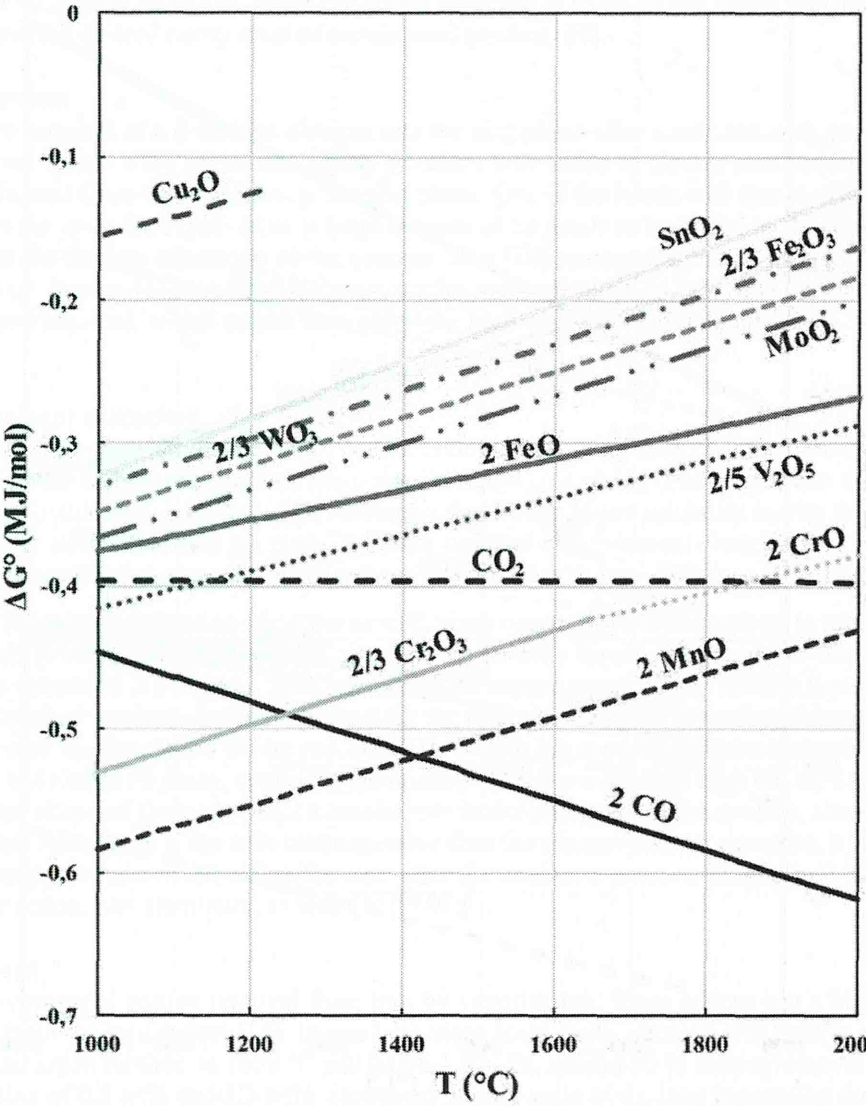

Figure 2. Ellingham diagram for oxidation of some unwanted elements typically present in steel scrap. Data from Hayes [7]. All reactions based on 1 mol $O_2$.

Alternatively to oxidation, elements can be removed by sulfidation. Figure 3 shows the Ellingham diagram for the sulfidation of some unwanted elements in the steel coming from scrap. For the drawing of the sulfidation Ellingham diagram, FactSage 8.1 was used, with databases FactPS, FTMisc and FTStel. Note that FactSage extrapolates data if no experimental data is available. Therefore, the sulfidation for the whole temperature range as presented in Figure 3 is not necessarily backed completely by experimental data.

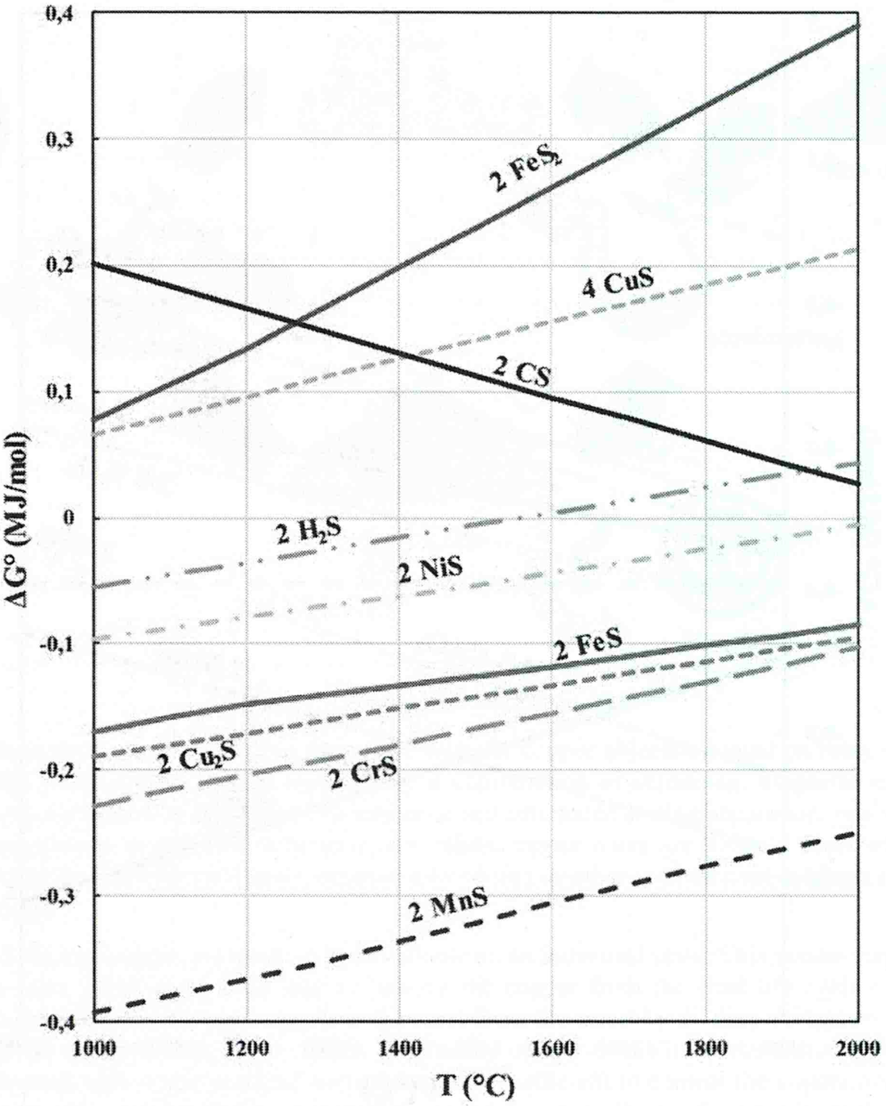

Figure 3. Ellingham diagram for sulfidation of some unwanted elements typically present in steel scrap. Data from FactSage 8.1, FactPS, FTMisc and FTStel. All reactions based on 1 mol $S_2$. $FeS_2$ and CuS formed from 1 mol $S_2$ and 2 mol FeS/$Cu_2S$.

Unlike for oxidation, sulfidation of copper is more likely than sulfidation of iron, meaning that sulfidation, in theory, can remove copper from iron. However, it should be noted that sulfidation of iron and copper are very close in the temperature range of steelmaking. Therefore, high iron losses can be expected when decopperizing the steel by sulfidation in an industrial process.

## DECOPPERIZATION METHODS

So far, different experimental studies have been published to find methods to remove alloyed or coated copper from steel. In the past, treatment with chemicals or metals, solvent extraction, gasification treatment, slag treatment, filtration, and leaching were investigated. However, none of these methods have been upscaled beyond lab scale because they were economically not attractive. These methods are briefly explained below.

### 1. Melt dilution

Melt dilution consists basically of adding a certain limited amount of scrap contaminated with copper (and other tramp elements) into the pure virgin iron bath. Melt dilution is considered as a satisfactory technique in times when plenty of virgin iron is available, and copper contents are low. In the future, when dilution is no longer sufficient, a more practical and realistic method would be copper removal before melting the scrap when larger amounts of scrap are charged [8].

As the average content of copper increases, more ore-based metallics (OBM) or hot metal will be necessary to dilute the contaminants and achieve the desired purity level of certain steel products [9].

### 2. Treatment with selenium

In the steel industry, the removal of a dissolved element into the slag phase after a reaction with another element is the most common refining method. Trials were performed where selenium was added to molten iron containing copper, resulting in $Cu_2Se$ formation. The formed $Cu_2Se$ then ascends to the slag phase. One of the issues with this method is that part of the added Se leaves the system as the toxic Se-vapor. Also, a large amount of Se needs to be added to decopperize the melt. Different laboratory studies observed the low efficiency of the process. Wei [10] removed a maximum of 12% of Cu from the melt, which is a low efficiency. Sandig [11] reported different studies with selenium on lab scale, but mentioned that "very high amounts of selenium" are required, which means that, given the high material costs, the method is not suitable for industrial application.

### 3. High temperature solvent extraction

High temperature solvent extraction has been tried for copper removal as well. In solvent extraction, a second liquid miscibility phase is created in which the copper can dissolve more than in liquid iron phase. The copper can then be removed from the second liquid phase by an oxide flux, like $B_2O_3$ [12]. Elements that have a lower solubility in iron than in copper, are suitable for this process, including silver, lead and bismuth. The high costs of these elements restrict their applicability in industry. Furthermore, these solvent extraction experiments have been performed with liquid pig iron ($C \geq 4$ wt%).

Aluminum can be used for solvent extraction of copper as well, since copper has a lower activity in molten aluminum compared to iron. However, in this process, the aluminum ($T_{melt}$ = 660 °C) forms a liquid phase and the steel ($T_{melt} \approx$ 1400-1600 °C) remains a solid, and the extraction is a liquid – solid interaction for copper transfer from solid to liquid. In a patent from 1992, a process is described in which molten aluminum is used for the removal of copper and other elements like tin and zinc. Iron loss was reported as one of the downsides of the process [13]. During lab experiments at a temperature of 800 °C, having a liquid aluminum phase and a solid Fe phase, copper concentrations in Fe were lowered from 0.6 wt% to 0.1 wt% [14]. It should be noted that the size and shape of the scrap plays a crucial role in the efficiency of the process, since the diffusion of copper will be the limiting factor. Aluminum is not only less expensive than the aforementioned elements, it is also already being used in the current steelmaking processes to deoxidize the steel after the converter process. Magnesium has been reported for low temperature solvent extraction, like aluminum, as well [15].

### 4. Gasification treatment

Several studies have investigated copper removal from iron by vaporization. Since copper has a higher vapor pressure than iron, it can be distilled from the liquid steel [16]. In one laboratory scale study, vacuum was used to remove the copper from the steel. In a vacuum induction furnace, at 1650 °C and 0.006-1.074 Pa, around 50 % copper removal was achieved with both an initial Cu concentration of 0.5 wt% and 1.5 wt%. However, in pilot scale trials, long processing times and Cu reversion by copper condensation on the walls were observed. Also, achieving pressures below 10 Pa is a challenge at industrial scale [8, 17].

Alternatively, further increasing the vapor pressure of copper in liquid steel by volatilization has been tested. When blowing $NH_3$ at 1627 °C and 200 Pa for 100 minutes in a 1 kg crucible, Cu concentration in the liquid iron lowered from 0.2 wt% to 0.0002 wt%, forming $CuN_x$ and CuH [15]. However, at industrial scale, maintaining this vacuum for a longer time is expensive.

Removing Cu from solid steel by chlorination and volatilization has been tested as well. Exposing the solid steel with Cu to chlorination gasses like HCl or an $Cl_2$-$O_2$ mix at 800-1100 °C, leads to the formation of volatile CuCl, which leaves the iron matrix as a gas. In lab experiments, steel could be decopperized from 1.0 wt% Cu to 0.05 wt% Cu. Air or $O_2$ is needed to oxidize the instable CuCl gas after it leaves the steel [8, 17].

### 5. Sulfidation

Since sulfur is the only element that will react with copper before reacting with iron, decopperization by sulfidation has been studied more frequently [16]. A good example is the sulfidation of copper with FeS, as illustrated in reaction (1) below.

$$FeS(s) + 2[Cu] = (Cu_2S) + Fe(l) \tag{1}$$

From reaction 1 it follows that a high copper activity in the melt and a low copper concentration in the sulfide slag is desirable for decopperization. A high C (preferably saturated) and P concentration in the melt enhances de-Cu efficiency, making hot metal more suitable for this method than refined liquid steel [18]. Since oxidation is unwanted during the sulfidation process, a reducing environment is required. However, for the EAF steelmaking route, there is no carbon saturated hot metal, meaning that extra carbon should be added before the sulfidation and removed again afterwards.

In lab experiments with an initial copper concentration of 12 wt% in liquid iron, at 1500 °C for 2-4 hours, a copper removal of > 90 % was achieved. An S:Cu ratio of more than 7:1 is required to achieve de-Cu [18, 19]. In other experiments, ZnS or $Na_2S$ were added, resulting in a copper removal of > 95 %. Also in these studies, initial copper concentration varied from 5-10 wt% [15].

The drawbacks of this method are that it does not show to be very efficient at lower initial Cu concentrations that can be expected when using typical obsolete scraps (< 0.5 wt% Cu). Also, the low-carbon scrap needs to be carburized first to decopperize, after which the remaining melt needs to be decarburized again. Furthermore, the sulfide slag that is formed in this process needs to be processed further.

### 6. Filtration

The method of filtration is based on ceramic and metal-melt interaction. Filtration requires that the formed Cu-rich phase (such as Cu-Zn intermetallics) adheres to a ceramic filter material instead of the Fe-rich phase. A proposed process is based on:

$$Zn + Cu \leftrightarrow [Cu_xZn_Y] \tag{2}$$

In the reported study, a spinel material, $Al_2O_3$-ZnO, is synthesized, and copper and zinc are aggregated. Filtration is done, and it can also remove non-metallic inclusions [11]. Research on this topic is still ongoing, but recently it was concluded that decopperization with $ZnAl_2O_4$, which is a different kind of alumina spinel ceramic, will not work [20].

### 7. Leaching

Copper can be dissolved in an aqueous lixiviant, and iron remains inert or passivates in ammonia-based solutions, as ammonia has the highest selectivity [16]. Leaching is a hydrometallurgical alternative treatment for copper removal in a solid state, as it presents a high separation yield and low energy consumption. For leaching, the scrap with high specific surface area should be submerged in a bath of a certain solvent.

In literature [21], ammonia is used as the leaching agent. Adding ammonium salt such as ammonium chloride to the solution enhances the copper dissolution. Leaching of copper in ammonia is done at temperatures of 25-80 °C. With sufficient stirring, 100 % of the non-alloyed copper can be dissolved in under 30 min during laboratory experiments. Higher temperatures and more stirring enhance the copper dissolution. Experiments with steel scrap with copper coating showed a 100 % copper removal under 15 min, without dissolving any significant amount of iron [21].

No information was found on experiments with polluted scrap and the effect on the decopperization capacity. Leaching with ammonia will only work on loose copper or copper coating. On alloyed copper in the scrap this method works in theory, but due to the slow Cu diffusion in steel this will not work in practice.

## DISCUSSION

When steel scrap needs to be decopperized, the easiest and most cost efficient method is to mechanically remove the loose copper from the scrap by commercially available methods like shredding and magnetic separation. The mechanical separation will be limited by the size reduction and the breakage of the Cu-steel binding. Fine shredding could be limited by the exponential increase of power consumption and cost increase. Only when that is not enough, the removal of still-physically-binding and coated or alloyed copper by chemical or metallurgical methods should be considered, because that will always be more energy intensive and at higher costs than mechanical decopperization. This is also the main reason why no commercial industrial methods are available now for the removal of coated and alloyed copper.

### 1. Copper coating

Removal of copper coating seems easier than removal of alloyed copper, since it can be done at low temperatures with Fe in a solid state. However, it is assumed that most copper that is present in scrap is either loose from the steel or alloyed. Only for scrap that has a high amount of coated copper, or copper that is attached to the steel in a way that repeated shredding will not remove it, non-mechanical decopperization of solid scrap is sensible. For scrap with enough coated copper, leaching and solvent extraction with aluminum seem the most viable decopperization methods. Chlorination gives good results for removal of coated copper as well, but the use of toxic chlorine is a disadvantage. All other methods discussed here require expensive reagents or prove to be ineffective at the lab scale.

For leaching, 100 % copper removal in less than 15 minutes at lab scale is achieved. Also, the ammonia-based leaching agent could in principle be cleaned and reused. The relatively low temperatures, 25-80 °C, do not form a barrier for industrial application either. An important next step would be scaling up the process to test if the high copper-removal rates can still be achieved in a short time. Another important aspect to test would be the use of post-consumer scrap, which will inevitably contain pollutions in the form of grease, oxides, other metals, etc. The leaching process should be able to deal with these.

Although solvent extraction with molten aluminum takes place at much higher temperatures than leaching, around 800 °C, the scrap remains solid during the decopperization process. At lab scale, the level of decopperization (0.6 wt% to 0.1 wt%) is less impressive than leaching. However, solvent extraction is still capable of removing most of the copper present. Like with leaching, upscaling the process and using post-consumer scrap are interesting and important next steps to test the viability of the method.

### 2. Alloyed copper

Since the removal of alloyed copper from steel is not done anywhere on an industrial scale, copper will continue to build up in future steel scrap over the recycling cycles. This will increase the need for the removal of alloyed copper from scrap in the future. Considering the increasing demand for circularity, also that of high-copper scrap, and the fact that a method that will remove alloyed copper will also remove all other forms of copper in scrap, an industrial method to remove alloyed copper from steel scrap will become increasingly wanted in the future.

According to the characteristics of the various decopperization methods, applicable for alloyed copper, that were discussed in *Decopperization methods* section, vacuum treatment and sulfidation seem to be the most viable method. Vacuum treatment proved to be able to decopperize liquid steel to 0.0002 wt% Cu at lab scale. For vacuum treatment at industrial scale, the need for a low vacuum (below 200 Pa) can be expensive, but it is possible. In current steelmaking processes, pressures as low as 50 Pa are achieved. A better kinetic understanding of the method is required to allow for an upscaled experiment.

The sulfidation method showed at lab scale to be able to remove >90 % of copper from liquid steel, with the remark that it shows lower efficiencies at lower copper concentrations. An advantage of sulfidation is that it could potentially be combined with the removal of other unwanted elements from steel that cannot be removed by oxidation. If such a combination would work, this would greatly improve the viability of an industrial sulfidation process. Such a process should be followed by a desulfurization process, as sulfur itself is an unwanted element in most steels too. Since sulfidation has to take place under circumstances comparable to BF hot metal (carbon saturated with a low oxygen activity), placing the sulfidation process prior to the hot metal desulfurization process in the BF-BOF route seems more feasible. This does require the addition of copper-rich scrap after the BF. However, this would lead to various practical constraints, like dilution, temperature control, etc. In the EAF steelmaking route carbon addition would be required, which could lead to an extra process step.

## OUTLOOK

Even if scaling up of the discussed decopperization methods would prove to be more efficient than expected and even if the average concentration of copper in scrap would double, removal of alloyed copper from steel will be an energy intensive and costly process. The cost-benefit of an industrial decopperization process will be optimized if only the scrap with high copper concentration is used, if the process can be combined with removal of other unwanted elements and if the removed copper (and other elements) can be regained. Furthermore, the industrial decopperization process will have to fit into the existing steelmaking route, meaning that the process time cannot exceed the process time of the BOF converter or EAF. The materials needed for the process, like solvents and reagents, should be available at reasonable costs and in large quantities. Finally, the process and its by-products should not lead to high risks for health, safety and the environment.

To anticipate on the possible future need of a decopperization process, Delft University of Technology in cooperation with Tata Steel Netherlands R&D, started the I-SCoRe project to bring the most viable decopperization process one step further in its development.

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