OXYGEN TECHNOLOGIES APPRAISAL FOR COPPER SCRAP SMELTERS

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Abstract:

Copper is one of the key metals for the nowadays industries and for the upcoming electrification, being produced by primary materials (mining, ore) and secondary sources (recycling, scrap). The global trend for recycling and lower impacts on environment are pushing for more scrap recovery and lower CO2 emissions by casting houses. One of the most important technologies toward the efficient use of fuel for copper pyro-metallurgical recovery is the combustion with oxygen, defined as Oxy-fuel, however that's not straightforwardly applied towards the complex needs to process different varieties of scrap feed. The main purpose is to illustrate how Linde's oxyfuel technologies interact with the melted copper bath, and to highlight new solutions aimed to give efficient process control thereby reducing copper smelters fuel consumption and increasing their productivity with better control and less emissions.

Keywords: Copper, Scrap, Pyrometallurgy, Oxygen, Hydrogen

Introduction:

Important metal for a variety of industries, possessing outstanding heat and, electrical conduction makes unique applications possible with Copper. Its strategic importance came from health applications up to wind generators with an expected exponential global growth going forward. To commercially produce this important metal, have two main sources: 1. Primary, extracted and produced by rich ores, including copper with different compositions (oxides, sulfides, etc.). It is a long process since the geological analysis up to the finished metal ready to be applied into a large range of products. 2. Secondary, involves the recycling and recovery of Cu from scrap source, refining it, and releasing again to the market.

Following the global increased demand for basic metals like copper, we are experiencing a global trend for green technologies and the minimum impact of all industrial sectors on environment with a reduction of carbon footprint. Associated with a steady increasing for prices of all basic metals, the secondary copper, been said above, is starting to gain more relevancy, once we have a recycling from scrap, a reduction on environmental impacts, reduction on carbon footprint and more efficiency to reach the same features the industry demand from primary metals, especially with high-grade of purity.

Toward to deploy new recovery plants, one of the challenges is to melt the metal with a high thermal efficiency, low emissions, and minimum chemical interactions to avoid contaminations. Linde is following the market trends and tailoring technologies for new market needs, including the pioneering of enhanced Oxy-fuel technologies for secondary copper smelters.

Copper Production

Copper (Cu) is one of the most available and valuable metals around the world, being one of Metals age 6000 and 1000 BCE (the Copper Age, the Bronze Age and the Iron Age). Found in metallic state or combined with different minerals, it is a reddish metal, malleable, ductile, and knowable by distinct features as an excellent electrical conductor and heat exchanger. Copper metal is produced by primary materials (ore from mining companies) or secondary materials (variable Cu scrap), also as by-product from recovery of other more valuable metals. It can be hardened using different metal alloys and mechanical and electrical properties can be affected and controlled by common gases such as oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), and sulfur dioxide (SO_2), since these gases are soluble in molten copper.

Copper Demand

The current Copper global demand is estimated by 28 million tons yearly, being 70% of that for electrical and communications applications according to the International Copper Association. From those 23 million of tonnes, 9.8 million are estimated as recycled Copper (figure 1) [1].

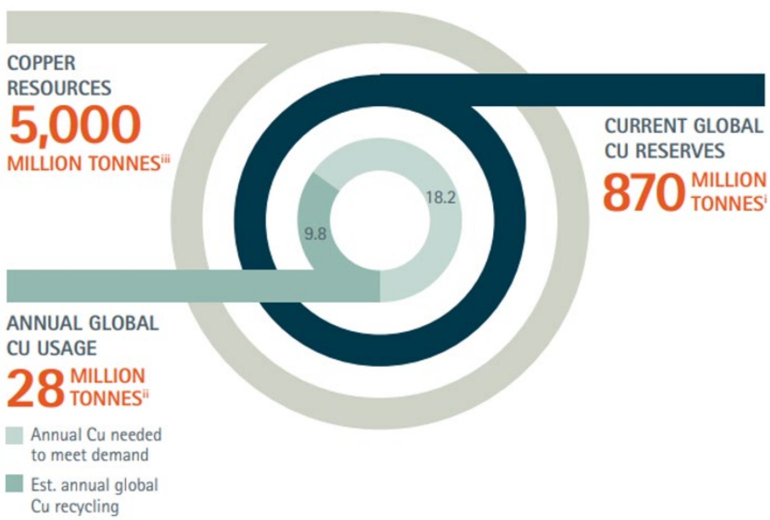

Figure.1. Global demand and reserves in 2020 [1]

Copper Scrap

Copper maintains its properties after melting and refining, thereby becoming a circular metal and its recycling an important economic activity. As pointed before, the whole copper chain depends on its recycling as about 30% of total input of copper. A typical copper scrap may be sorted by its quality, alloy, and impurities, and usually is classified in different grades in different markets referring to its value. Some common classifications for North-American market are [2]:

a. Bare Bright Copper
   Is that clean and bright as a new copper product, usually with 99.9% Cu and should be not thinner than 16-gauge (0.05 in or 1.29 mm) and free of contamination such as

surface oxidation, insulation, and all other non-copper attachments. Bare bright copper comes from power cables without the insulation. Some markets refer to this grade and copper n.1 as Pure Copper or Honey Copper.

b. Copper n.1 (or #1 copper)
It has the same quality as bare bright copper but usually comes as tubes, pipes and other wires not thinner than 1/16 in. It needs to be free of non-copper attached. Usually is sold in form of clean tubes and pipes.

c. Copper n.2 (or #2 copper)
Usually with a minimum of 94% of copper content (usually 94-96%) is the n.1 with contamination (dirty) and including tin-plated. Also, not thinner than 1/16 in. It is sold as plumbing scrap with solder, paint, dirties, as well as wire, oxidized copper, copper-bearing and tin plated.

d. Light Copper (or #3 copper)
Should have at least 92% Cu content and comes and different forms usually as thin sheet. It should be free of excess of Lead, tin, brass and bronzes, iron and oil (greases).

Other classifications are used for different scrap dealers toward valuation for each scrap quality to be sold or bought by them. Difference between lower grades as #3 or light copper and the bare bright prices reaches more than 30%. Figure 2 shows us a typical copper flow as in year 2018 and all scrap input throughout the supply chain including the End-of-life (EoL) scrap.

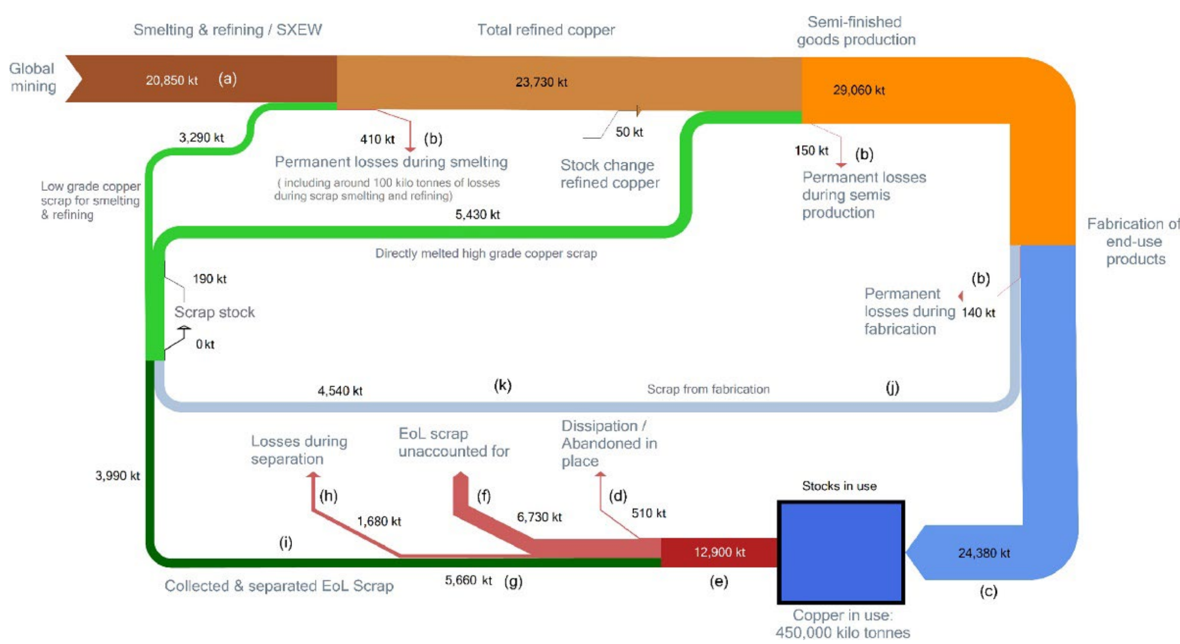

Figure 2. Estimated global copper flows in the year 2018 [3,4].

Secondary Copper Process

A typical copper recovery process uses rotary or reverb furnaces to melt, refine and tap the recovered copper from scraps. The TSL (Top Submerged Lances) and TBBS (Top-Blown Bottom-Stirred) are the most common equipment for Cu scrap recovery (figure 3).

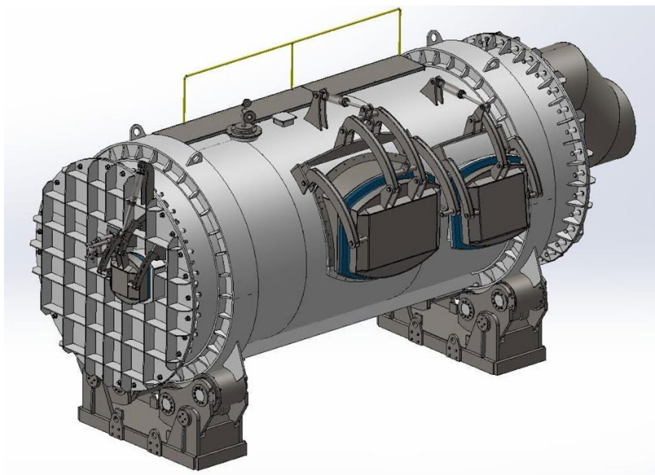

Figure 3. Typical design for Scrap Melting and Refining using TBBS.

First, the scrap is sorted from different grades and fed into the furnace to start the melting process. The loaded material used to have a low density. Therefore, a previous Copper pressing step is important to guarantee more velocity during the charging step (more mass, low volume each feed step). The charging and melting step usually are responsible for more than 40% of a common Copper batch time, and around 70 to 80% of all energy consumption (figure 4).

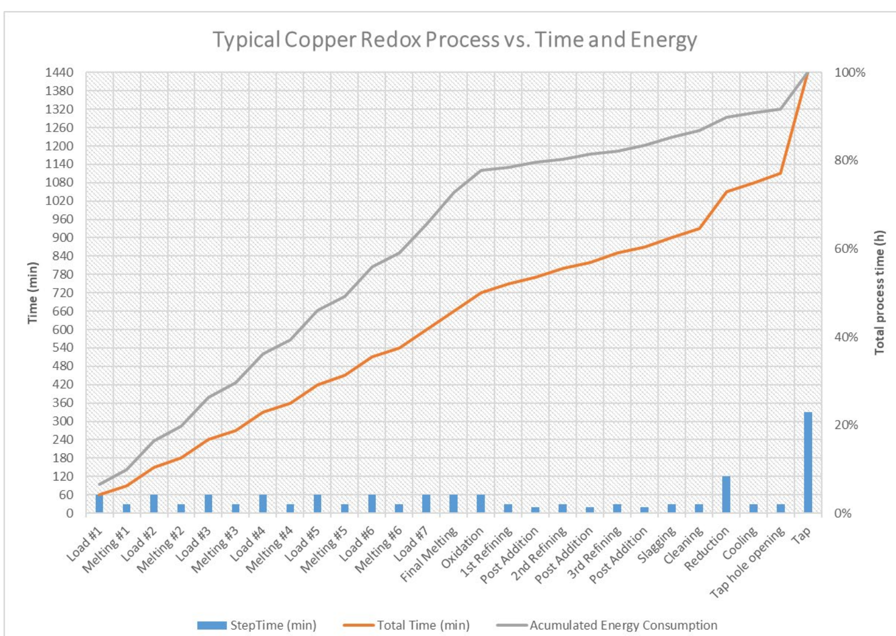

Figure 4. Common steps and for secondary copper recovery.

Dirty scraps, with high content of other metals, needs an additional step of oxidizing, to remove the metals through an oxidation reaction, it means a demand for an additional oxygen into the furnace atmosphere and the melted copper, as well an additional oxygen to burn the VOC and other fuel contents added into the furnace coming from scrap dirty.

$$M(s) + O2(g) = MO2 \text{ (not balanced)}$$

After that, the copper needs to be refined, and all copper oxides and oxygen dissolved (5000-8000 ppm) reduced to at least 400 ppm. The best technique is to add carbon as reductant agent bubbling Natural Gas or feeding Charcoal. The reaction occurs as below:

$$C + O = CO$$

$$CO + O2 = CO2$$

$$CO + CuO = Cu + CO2$$

During the reduction step, any additional oxygen into the internal atmosphere competes with the reducing reactions. The most common technique is lancing the reductant agent underneath the bath surface (figure 5).

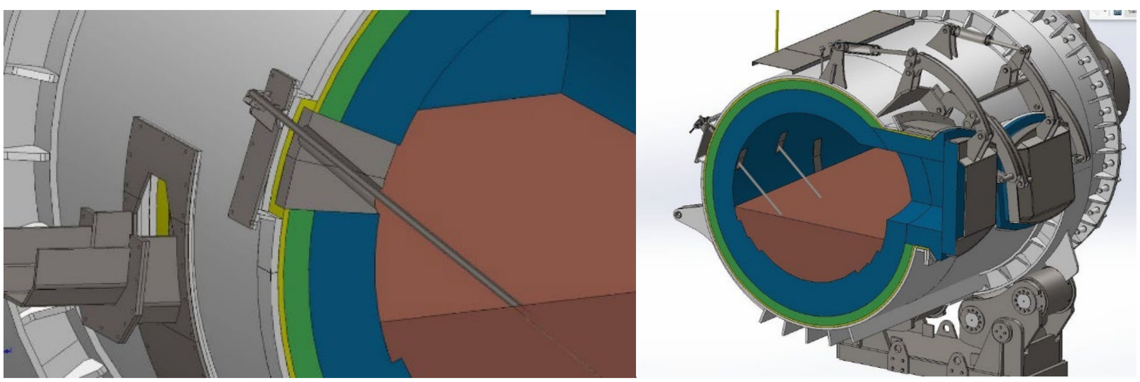

Figure 5. Model to simulate lancing step into a copper scrap furnace.

And finally reaching a specified composition, around 99,9% of Cu purity with a sum of 1000 ppm for all other impurities and 200 ppm maximum for the dissolved oxygen, the metal is ready to tap. The tapping step with a specified material is the last step into the furnace and care must be taken to maintain the metal composition through atmosphere composition control.

Oxyfuel

As widely known, combustion is a chemical reaction between chemical elements releasing energy, technically speaking an oxidation reaction which product is an oxidized element thru an exothermic reaction. For combustion purposes we need at least 4 elements: Fuel (chemical component to be oxidized yielding energy during the reaction), Oxidant element (chemical component able to reduce its chemical potential), Heat to provide the ignition or the minimal energy needed to start the reaction and mixing to maintain the continuous reaction between fuel and oxidant. It’s common to see a fire triangle as a safety or fire suppression training, that doesn’t include the fourth element: mixing. Fuels can be solids, liquids, gas, as well a mixing of more than one phase while we have commonly the oxygen from air as an oxidant.

Oxyfuel is the name given to combustion process using pure or enriched oxygen (O2) as a comburent instead of air, containing 20.9% of O2 in volume. Removing the Nitrogen (N2) from combustion reaction, is it possible to reduce losses due to avoid a waste of energy heating the Nitrogen, normally departing the reactor uncaptured. For many processes, it's still important keep the Nitrogen as a heat carrier, and convection agent, but for all the others, at temperatures as higher as 900 deg. C, the heat transfer mechanism become predominately irradiation and that's enough to start its thermal step, including for many of smelters the melting step.

Figure 6 shows the calculated fuel savings as a function of flue gas temperature, comparing Air-fuel and Oxy-fuel combustion process. The curve shows us that above 900 deg. C, 30% of savings is achievable using Oxy-fuel while above 1300 deg. C more than 50% can be saved comparing the efficiency of both technologies. That happens because the energy is lost through the flue gas as heated nitrogen.

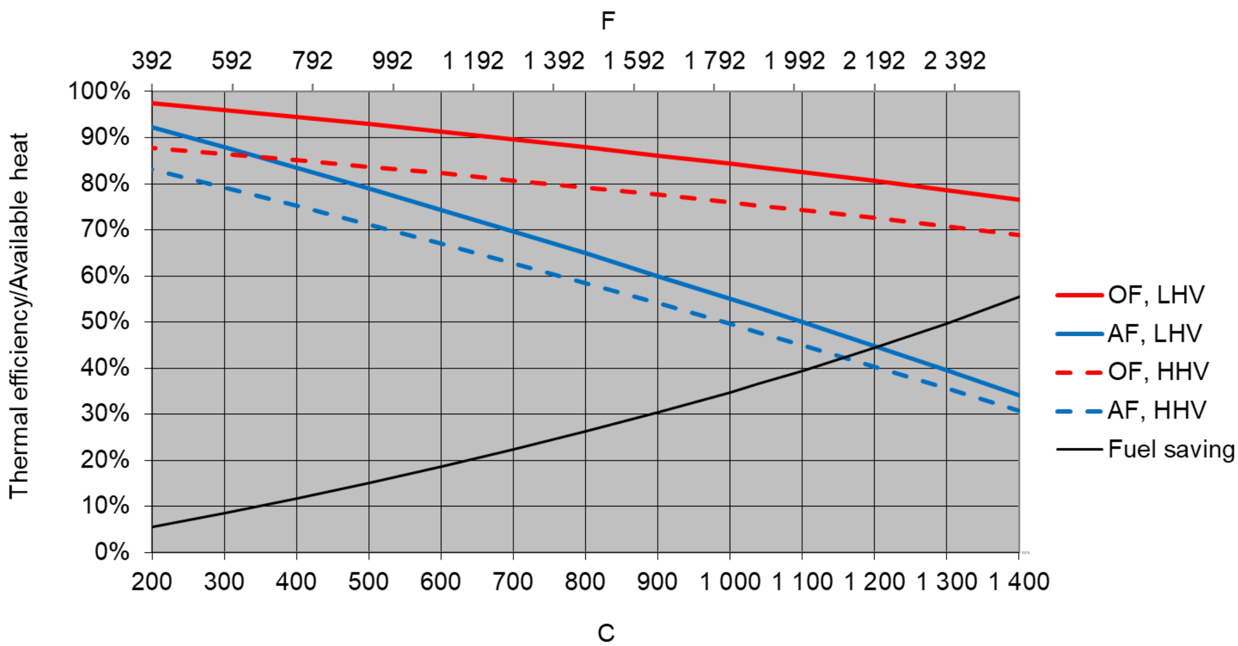

Figure 6. Thermal efficiency for Air-fuel and Oxy-fuel for different flue gas temperatures.

According to Buchholz, A., Rødseth, J., heat transfer is mainly dominated by radiation, being more than 90% for higher temperature process, and Stefan-Boltzmann law of radiation express the radiation heat transfer rate as a straight-forward dependent of the emission source temperature [5], as described below:

$$\dot{Q} = \sigma.\varepsilon.A.T_S^4 \ \ (W)$$

Once the oxygen proportion in the comburent increases, so increases the adiabatic flame temperature. For example, for Natural Gas or Methane, 40% higher (1938 deg. C with air vs. 2754 deg. C with 100% O2). Thereby, using a higher radiative flame, with higher adiabatic temperature, results in a quicker heat transfer, four (4) times higher comparing both cases for Methane.

An example of the increased heat transfer by gas radiation at 1000 deg. C (1800 deg. F) using different proportion of Oxygen as a comburent is presented below at figure 7.

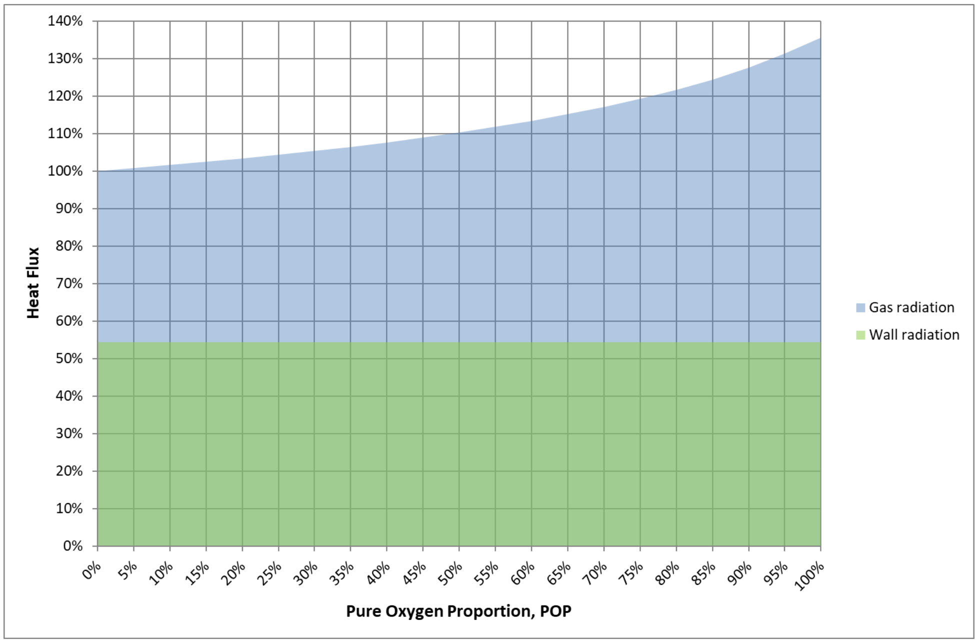

Figure 7. Heat transfer changes by radiation in function of different oxygen content as oxidant [6].

Each 1 MWh of Methane (CH4) at air-fuel burner running with no air excess (lambda = 1.0) has the follow typical flue gas in wet and dry basis, with an overall efficiency of 50% considering the flue gas at 1000 deg. C, meanwhile the same 1 MWh thru oxy-fuel burner has 76% of thermal yield.

COMPOSITION WET BASIS		**Air-Fuel**	**Oxy-Fuel**
CO_2	%vol	9.5	33.3
H_2O	%vol	18.9	66.7
SO_2	%vol	0.0	0.0
N_2	%vol	71.6	0.0
O_2	%vol	0.0	0.0
COMPOSITION DRY BASIS		**Air-Fuel**	**Oxy-Fuel**
CO_2	%vol	11.7	100.0
SO_2	%vol	0.0	0.0
N_2	%vol	88.3	0.0
O_2	%vol	0.00	0.00

Figure 8. Flue gas from stoichiometric combustion of CH_4 with air (Air-fuel) and O_2 (Oxyfuel).

At the end, replacing air to pure oxygen for combustion leverage a plenty of benefits as summarized below:

i. Increased Melt Rate per unit surface area
ii. 30-50% reduction of specific energy consumption for the referenced process
iii. 72% reduction in off gas volume per energy unit

iv. 80-85% reduction in off gas volume per ton of Copper
v. Reduction of CO2 emissions
vi. Reduction of NOx emissions
vii. Unchanged or improved recovery of Copper
viii. Unchanged refractory wear per ton of Copper processed
ix. Reduced noise

Linde Technologies for Oxyfuel applied for Copper Scrap Furnaces

Once the Copper reaches its melting point around 1080 deg. C, it needs at least 146 kcal to heat and smelt each kg (170 kWh/tonnes) of copper, in addition to the process losses such as flue gas, refractory lining absorption, over temperature heating, etc., it reaches around 700 kWh/tonnes Cu scrap from room temperature to 1200 deg. C operating with a common air-fuel burner. The first step to reduce the energy demand is to reduce the waste of energy downstream with the flue gas. With 1200 deg. C and no heat recovery, it means a waste of at least 62% of energy thru the flue gas that can be translated with higher costs and emissions and less productivity.

Available technologies for heat recovery are widely known meanwhile the oxyfuel technologies are avoided due to the specific contamination concerns with oxygen for copper. The copper for a wide range of applications need to keep the dissolved oxygen below 200 ppm (w/w), so the use of pure oxygen as a comburent have been evaluated with caution.

On one hand, the refinery producing secondary copper demands a high amount of energy to be solved by use of pure oxygen as a comburent, on the other hand its use may contaminate the metal through incorrect the application of the technology. Traditional oxy-fuel burners produce very intense high flame temperatures that can potentially cause hot spots, leading to concern regarding refractory damage, oxidation (such as in aluminum melting) and volatilization (such as in glass melting) and high NOx emissions

Notwithstanding, Linde have been applying Diluted Oxygen Combustion – DOC technology and your patented burners, in addition to new technologies of image analysis (OPTIVIEW^{TM}) and gas analysis (OXYSENSOR^{TM}) to reach the best results from an oxy-fuel burner while it has a low temperature flame, dilution, and enough features to melt it with no harm to the copper bath, its composition, refractory lining, environmental and costumers' productivity.

Diluted Oxygen Combustion

DOC technology is a low-peak flame temperature and low-NOx oxy-fuel combustion process using in-furnace recirculation of flue gas therefore it provides a recirculation from the combustion and other interiors gases, diluting the fuel, comburent and the flame with the inside atmosphere, reaching up to a flameless mode [7,8]. Figure 9 shows different temperature using the in-furnace recirculation technique, or the aspirating burner, demonstrated that the peak flame temperature of oxy-fuel flames could be reduced even below those promoted by conventional air-fuel burners.

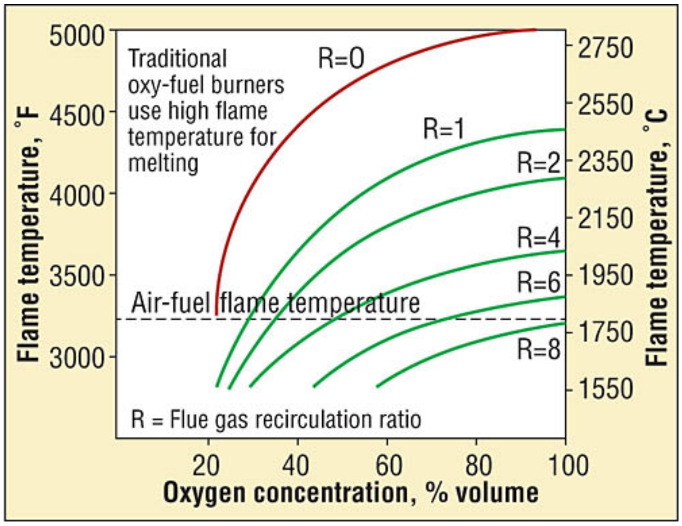

Figure 9. Flame peak temperature using Natural Gas for different recirculation ratios [7].

The performance of DOC technology has been measured under laboratory and industrial conditions encompassing both natural gas and coke oven gas firing, and a wide range of furnace temperatures and nitrogen levels that simulate air infiltration [8].

Using the DOC technique, the JL (Jet-lance) burners and LTOF (Low-temperature oxyfuel) burners provide different zones with just one burner. As shown in figure 10, the main burner with a rich content of fuel, and lances with a high-speed discharge of oxygen are used to promote the aspiration and recirculation from all furnace gases with the flame, giving flexibility, homogeneity, and a reduction of adiabatic flame temperature giving greatly reducing NOx formation.

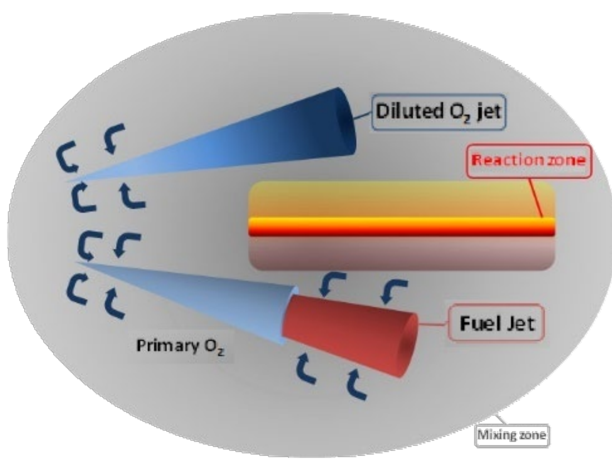

Figure 10. JL's flame profile with 2 different zones (fuel rich and oxygen rich).

Figure 11 is exemplifying a common JL burner design. The burner has a compact design, made with stainless-steel or special high-temperature resistant Nickel alloys, not water-cooled, and mounted into ceramic blocks (customized) with nozzles designed to control both discharge speeds (fuel and oxygen lance), promoting enough recirculation inside the furnace, aspirating all inside atmosphere and diluting the high temperature flame as mentioned before.

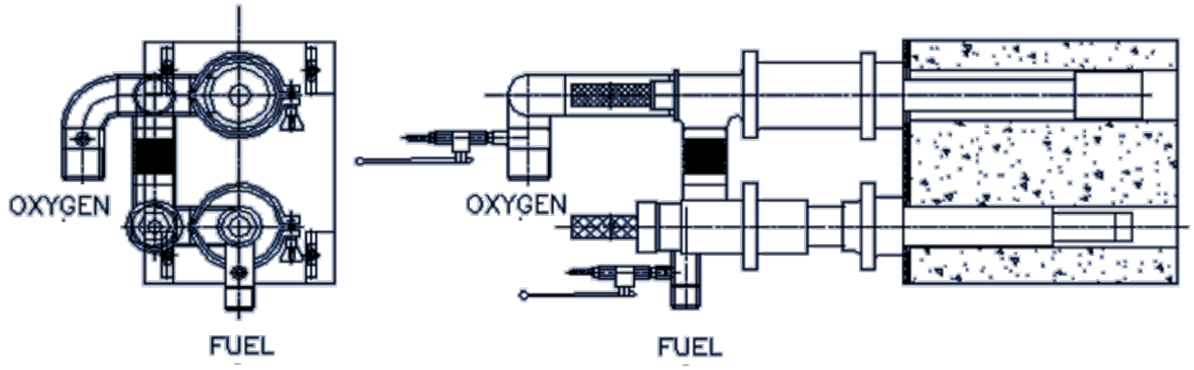

Figure 11. Typical design for a JL burner with lance on top (block with 11 x 16 in or 270 x 400 mm)

The JL is usually installed at side ends, if possible, counter current with flue gas, aiming the free chamber above the copper surface. No angles are required and the flame flow in parallel to the melted copper is preferable to avoid the flame impinging cold material or lining, diverging the flame (figure 12).

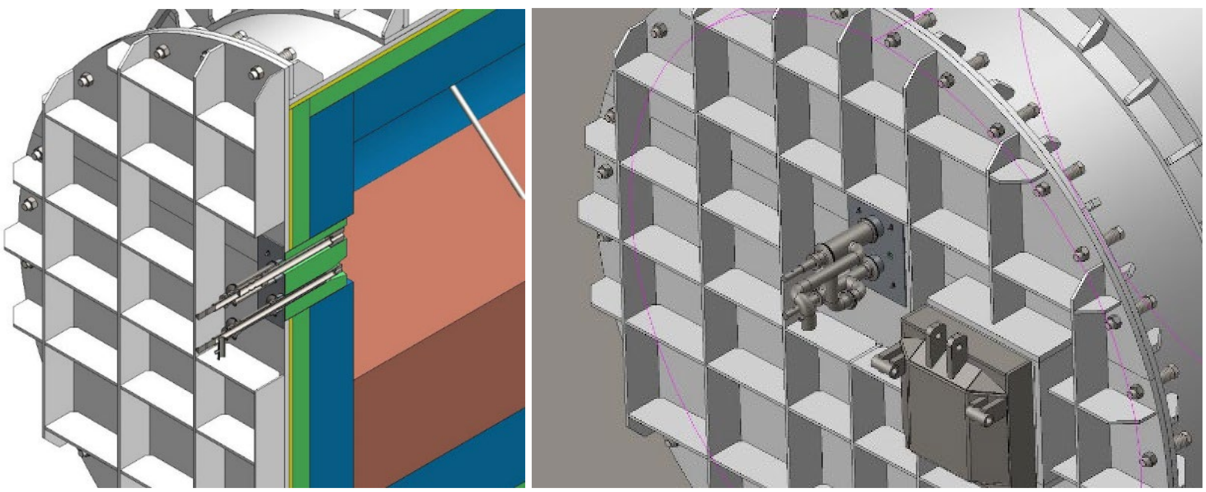

Figure 12. JL positioned at side end of copper secondary furnace.

For the melting step, use of JL with Lance on top is enough in the most case to reach the melting rate and low fuel consumptions, the staging ratio between 25-75% give the burner enough flexibility to reach longer flames and lower NOx emissions, but not enough for the chemical goal to increase the dissolved oxygen at the end of smelting step. It happens because the JL with Lance on top creates that fuel rich zone, though a reductant atmosphere, protecting the Copper surface of all free oxygen able to be dissolved. Meanwhile, the Lance on top keeps the free oxygen far from the Copper surface that's the major issue during the last steps (refining and tapping), protecting the copper surface and keeping the dissolved oxygen amount around 200 ppm as required for the final and downstream process downstream. Usually, Cu+Ag higher than 99.90%, all impurities sum less than 1000 ppm, O2 between 150 and 220 ppm and Copper temperature between 1110 and 1120 deg C. Despite of all other elements, Pb may be added.

For advanced systems and customer requirement, Linde can provide a flexible JL that can operate with switchable Lance on the top or bottom position, changing by operator or PLC command as soon as the step needs oxidation or reductant behavior (figure 13).

Figure 13. 7 MMBtu/h (2MW) flame with flexible JL (left: Lance on bottom, righ: Lance on top).

Studies using the JL with Lance on bottom position show us a quick oxidation during the melting step reaching 5,000-10,000 ppm at the end of that process, improving the refining quality and time once it has almost all other metals impurities oxidized by the high amount of dissolved oxygen (e.g., Fe content must be less than 30 ppm to avoid blocking the spout and Te, Bi, S less than 15 ppm to avoid fragilization of copper bar). Figure 14 shows different oxidation grades using air fuel burner, JL (lance on top) and JL (lance on bottom) in actual Copper process during 30 different batches in a row for each process. It is possible to see a low concentration using JL with lance on top, at the meantime, the lance on bottom position has as much interaction as the old air-fuel burner for a 90 tonnes Cu scrap furnace. Outliers are common and depending on fan speed, scrap quality, time with opened door (drawn air) and others.

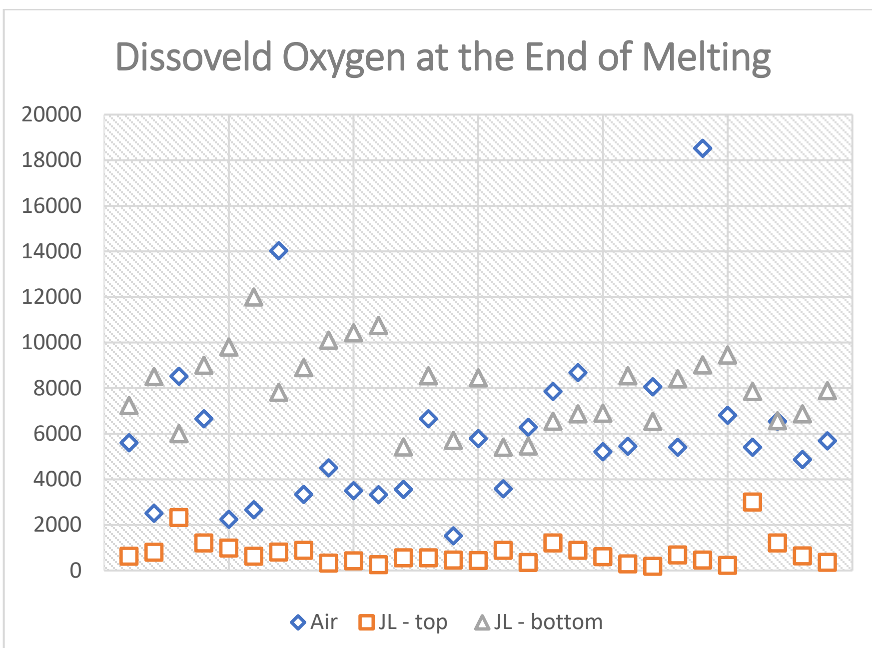

Figure 14. Different dissolved oxygen using Air-fuel, Oxy-fuel (JL-Lance on top), (JL – Lance on bottom)

Although the DOC technology seems enough to solve the copper and oxygen issues, deploying technologies such as OPTIVIEW ™ and Oxysensor™ give to cast houses a smart condition to control several kinds of scrap, with different composition and extract the most from each load material.

Image Analyses System - OPTIVIEW ™

As mentioned before, copper scrap is sold in different forms and qualities, being the oxidation of non-copper contaminations and controlled burn of all combustible contaminants, VOC an important step aiming an easier chemical refining.

For that reason, the OPTIVIEW ™ technology fits the need to control the additional fuel content flowing thru the flue gas and correct the addition of oxygen automatically (an open flame is needed, or a view of flue gas and flame thru the exhaustion system).

OPTIVIEW ™ Image Analysis System is as its name says a technology that automates combustion control by modulating burner fuel and oxygen rates and supplemental oxygen injection into the TRF using real-time flame monitoring (image). The system minimizes the occurrence of exceedances of CO and reduces demands on operators [9].

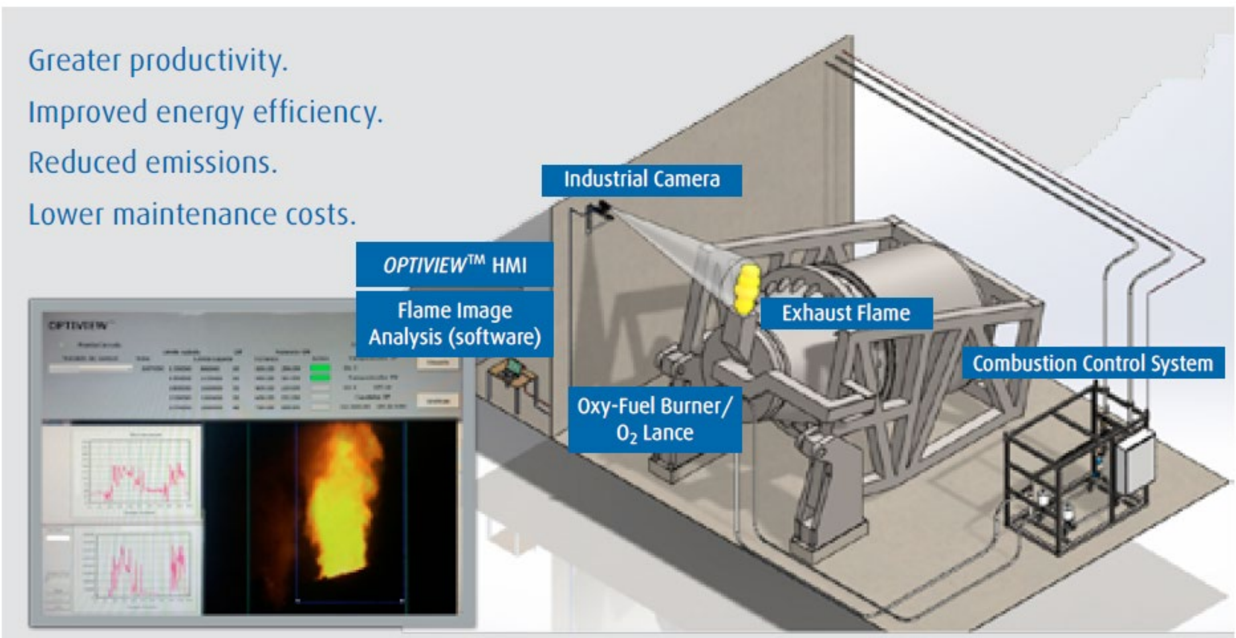

Figure 15. Typical OPTIVIEW installation and layout as developed for Tilting Rotary Furnaces.

The main goal is to provide enough oxygen to burn remaining fuel at flue gas inside the furnace. The figure shows us on left the operation screen with a chart of how much volatiles and fuel the flue gas has and its trend changing by oxygen modulation into a loop control (High colorspeck > more oxygen > low colorspeck > less oxygen > high colorspeck >…). On the right side the OPTIVIEW camera is installed focusing into the window opened at post-combustion chamber of copper scrap furnace.

Figure 16. OPTIVIEW™ operation screen (left) and installation at copper furnace gas ends (right).

Oxysensor™

The leakage of oxygen from atmosphere to the furnace or an unbalanced reaction with the oxygen and fuel from the burner, quickly can change the copper composition after refining, on reducing or tapping steps. Linde have deployed the Oxysensor™ as a tool to control the oxygen at atmosphere and flue gas, automatically changing the ratio between fuel and oxygen to keep as lowest amount of free oxygen as possible, keeping the copper composition, saving fuel, and improving the process control and quality.

Figure 17. Oxysensor™ installation at copper furnace. Left: Probe. Right: Oxysensor™ cabinet/unit.

***CoJet®* Coherent Jet Technology**

Additional technology for the oxidation and reduction process have been developed for the copper market, aiming to substitute the tuyere operation to add oxygen, compressed air, natural gas, or others reductant gases using a Coherent Jet – CoJet® injector, operating not only as a lance, but also as an oxyfuel burner. Linde pioneered the development of *CoJet®* Coherent Jet Technology for steelmaking and extended its development and application to copper-making furnaces.

The introduction of Linde's CoJet® Coherent Jet gas injection technology 25 years ago, was a significant step in effectively injecting chemical energy in electric arc furnace (EAF) steelmaking. This breakthrough technology was the first to introduce the concept of fixed wall mounted injectors, with each injector designed to perform multiple functions including oxyfuel burner, oxygen lancing, post combustion, and carbon injection. Figure 18 shows a CoJet® injector and its installation in the EAF. [10]

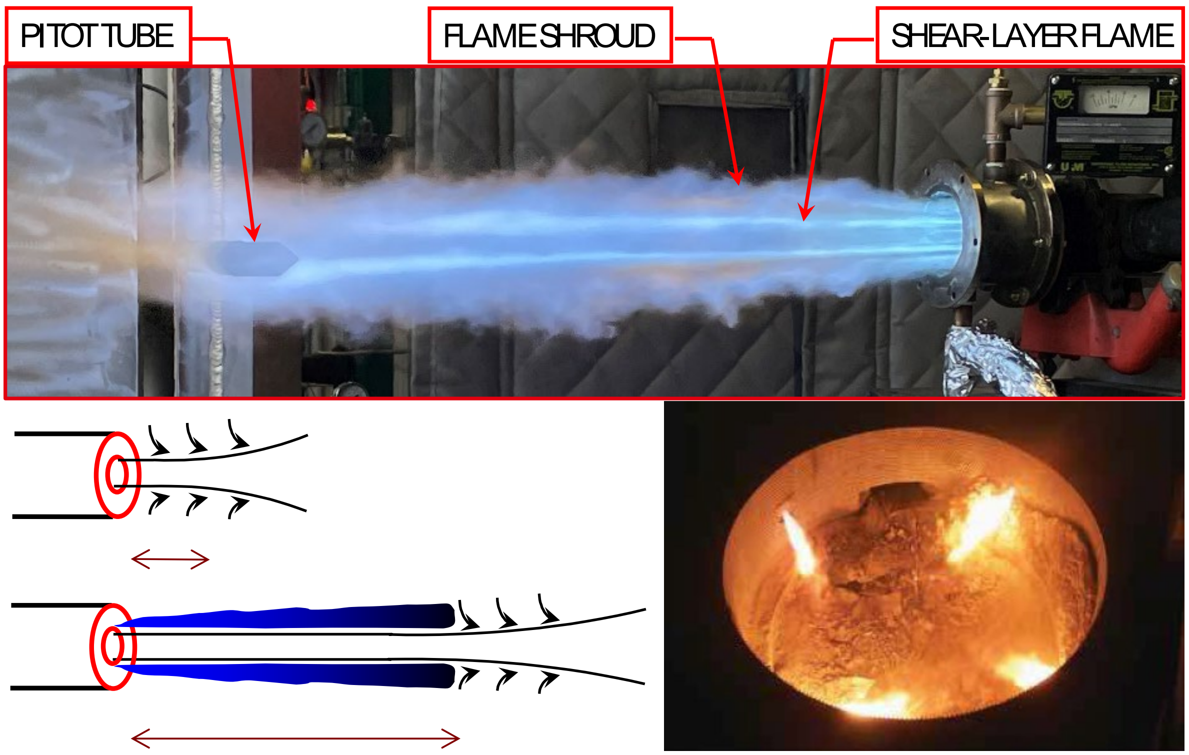

Figure 18. Top – O2 *CoJet®* technology firing natural gas; Bottom Left – flame shrouding concept; Bottom Right – 165T DC EAF [10].

The *CoJet®* technology was developed by the former Praxair company, which merged with Linde to form Linde plc in 2019. Exploratory research on supersonic gas jet behavior by Linde's senior corporate fellow Dr. John Anderson and coworkers led to the concept of flame shrouded supersonic jets, which become coherent and maintain their exit velocities and momentum rate over long distances. Dr. Pravin Mathur and coworkers first commercially applied this know-how to the EAF (ca. 1996), culminating in the AIST 2022 Tadeusz Sendzimir Memorial Medal for this remarkable contribution [10]

An optimum flame shroud extends the length of a Mach 2.0 supersonic oxygen jet in ambient air from ~ 15 nozzle diameters to about ~70 nozzle diameters. In an EAF this laser-like oxygen jet can be positioned well above the bath in the sidewall of the furnace and still carryout effective bath lancing. The coherent oxygen jet impinges and penetrates the slag and into the molten steel bath wherein the concentrated momentum of the oxygen jet dissipates as mixing power and distributes the oxygen as fine bubbles, providing deep penetration and effective slag-metal mixing and results in high efficiency decarburization [10].

Using the *CoJet®* Technology as a Top-Lance operation we have the Oxyfuel burner mode for heating melting accretions and recovering the furnace volume and enhancing cold scrap melting. Using it as Oxygen-Nitrogen (O2/N2) lance for oxidation and desulfurization (primary copper production), as Natural Gas-Nitrogen (NG/N2) lance for reduction (poling or deoxidation) processes and with Nitrogen (N2) for stirring (figure 19).

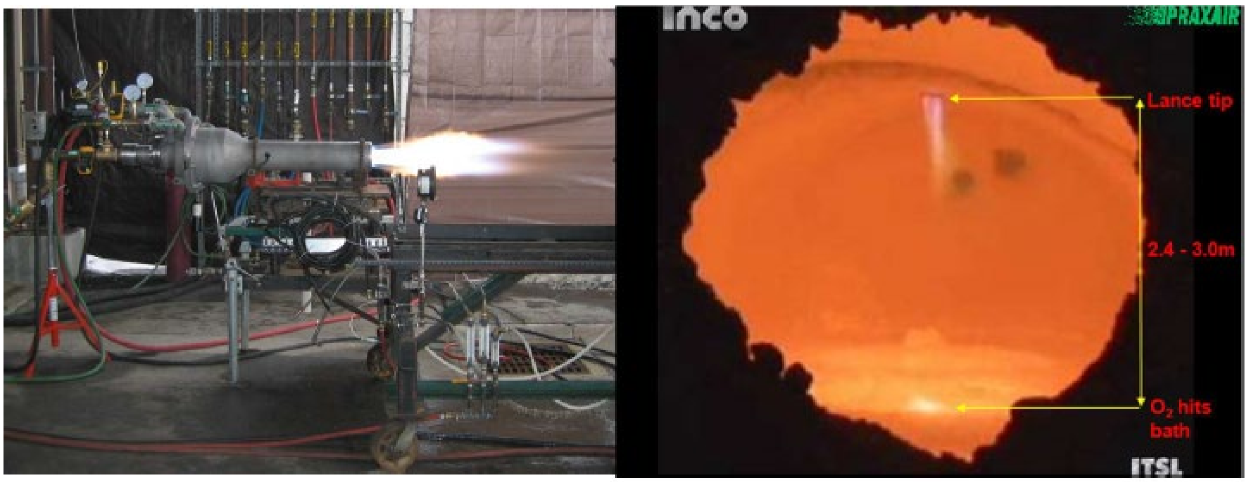

Figure 19. CoJet for copper been tested at Linde Technology facility in Tonawanda and in operation at Copper Furnace (Inco's MK Reactor) [10].

CONCLUSIONS

The technologies discussed in this paper are not only a specific oxyfuel technologies or hardware, but in addition, Linde also provides tailored solutions toward overcoming the latest challenges in copper-making and others, using its capabilities, Technology centers and professionals to develop new applications to control different combustion process and emissions. The staged flame highlighted here can create different zones between fuel-rich or oxygen-rich, matching the process needs for each step and supporting customers' process improvement, including an increased thermal efficiency without increasing metallic losses with more slag formation.

The staged flame technology, using JL burner, is presently installed in many different secondary copper furnaces around the globe, including the United States, Canada, Brazil, India, and China, delivering different benefits as significant fuel savings and production boosting, and CO2 emission reduction. The low maintenance, non-water cooled, reduced size and high efficiency make the Diluted Oxygen Combustion (JL-DOC) a great technology consideration for all upcoming projects using direct flame to recovery copper scrap.

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