Solar thermo-chemical process assisting a pressure oxidation process for co-production of electricity and metal

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Abstract –*The mining industry is looking at the use of solar energy to address issues related to highly variable energy prices, falling ore grades, and increasing concern about the industry's carbon footprint. The pressure oxidation of ore sulfides is an economic alternative to the smelting process because it has the potential to reduce energy consumption and treat low-grade ores. In the pressure oxidation of ore sulfides, the purity and utilization of oxygen are key factors. Indeed, oxygen production and consumption constitute the major operating cost of the pressure oxidation process. Solar thermo-chemical looping processes have been identified as one of the most efficient pathways for the production and storage of oxygen. This study investigates the integration of a solar thermo-chemical looping process with a pressure oxidation process to treat ore sulfide and produce electricity. The analysis shows that the temperature of the cold storage tank has a strong influence on the performance of the complete system. The increase in the cold tank temperature results in a sharp decrease in the size of the receiver. This reduce the investment costs for both the solar receiver and the heliostat field. For the considered case, the useful heat of the solar receiver is 3.7 MWth when the cold tank temperature is set at 100°C. If the cold tank temperature is set at 400°C, the required useful solar heat is about 3.1 MWth and the nominal output of the gas turbine is 0.56 MWe. The analysis showed that about 80% of the useful solar heat can be used to generate oxygen when the temperature of the cold tank is as high as that of the reduction reaction.*

Keywords: *Solar thermo-chemical, pressure oxidation, energy storage, oxygen production, oxidation / reduction, solar mining process.*

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Nomenclature		*subscript*	
d	diameter	c	compressor
h	enthalpy	ele	electric
ṁ	mass flow rate	ge	electric generator
P	pressure	in	inlet
Q	heat	mec	mechanic
t	time	out	outlet
T	temperature	t	turbine
W	work	rec	receiver
x	conversion	red	reduction
η	efficiency	st	storage

I. Introduction

Conventional mining processes depend on hydrocarbon resources for producing metals [1]. These processes are highly energy and carbon intensive [2]. The issues of fossil fuel depletion and climate change have pushed scientists to develop innovative solar mining processes [3-6]. Concentrated solar technology offers the option of converting solar energy into heat, electricity and chemical forms. Processes that make use of solar heat to drive high temperature endothermic chemical reactions are known as solar thermochemical processes. Solar thermochemical processes has huge potential in industries like metal [7]. Previous published studies showed that metals can be produced from their metal oxides, using solar thermos-chemical process, mainly by three methods: Direct dissociation, Carbothermal reduction process, and Methanothermal reduction process [7]. The implementation of one of the three cited processes require changes in the existing mining processes. However, suitable use of solar energy in the existing mining processes should has relatively low investment costs to be accepted by the mining industry. We propose the integration of a solar thermos-chemical process into an existing solar mining process, known as, pressure oxidation process (POX). The existing POX require just minor changes to be coupled with the solar process. In the POX an autoclave reactor working at high temperature and pressure is used to oxidize ore sulfides [8, 9]. High-pressure oxygen is introduced into the autoclave in such a way as to maximize the dissolution of the gas into the solution phase. Once dissolved in the solution, oxygen reacts exothermically with ore sulfides to produce oxide minerals. The purity and the utilization of oxygen are key factors in the POX since oxygen production and consumption constitute the major operating cost of the process [10]. This study investigates the integration of a solar thermo-chemical looping process (SCL) with a POX to treat ore sulfides and produce electricity.

II. Description of the complete system

Typical industrial POX is illustrated in Figure 1. Oxygen is feed to the autoclave reactor to reacts exothermically with ore sulfides and produce oxide minerals. The first commercial POX was implemented to treat refractory gold while the second one was implemented to treat copper concentrate [9]. In the present study, solar energy is used to generate storable electricity and oxygen thanks to the two storage tanks. The particles are stored in the hot tank. They are then sent to the air reactor where Cu2O is oxidized to produce heat (4 CuO(s) + O2(g)=>2 Cu2O(s)). CuO/Cu2O redox pair is selected because it has a high oxygen transport capacity and is relatively cheap and the driving force of the redox reactions is the change in the pressure of oxygen in the gas phase [3]. To promote the reduction reaction in the solar receiver, steam is used to control the partial pressure of oxygen. The vitiated compressed air in the air reactor is expended in the gas turbine cycle to produce electricity. The O2/steam mixture is sent to the POX tank where it is used to oxidize ore sulfides.

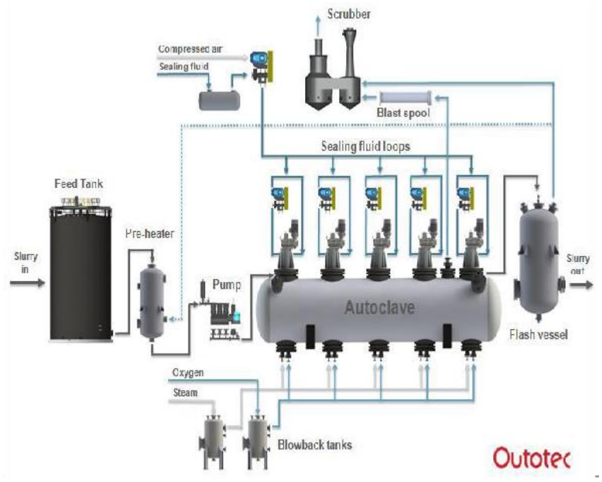

Figure 1. Typical pressure oxidation process [10]

The proposed SCL-POX to treat ore sulfides and produce electricity is depicted in Figure 2. It consists mainly of a solar particles loop, a modified gas turbine cycle, and a POX tank. The solar particles loop mainly consists of a solar reductor, a hot storage tank, a cold storage tank, and an air reactor. A mixture of particles composed of CuO as the active ingredient and $MgAl_2O_4$ as the inert support is used as the working fluid of the SCL process. Initially, the $CuO/MgAl_2O_4$ particles are sent to the solar reductor where CuO is reduced to Cu_2O ($4CuO_{(s)}$ => $2Cu_2O_{(s)}$ + $O_{2(g)}$). Next, the particles are stored in the hot tank. They are then sent to the air reactor where Cu_2O is oxidized to produce heat (4 $CuO_{(s)}$ + $O_{2(g)}$=>2 $Cu_2O_{(s)}$). CuO/Cu_2O redox pair is selected because it has a high oxygen transport capacity and is relatively cheap and the driving force of the redox reactions is the change in the pressure of oxygen in the gas phase [12].

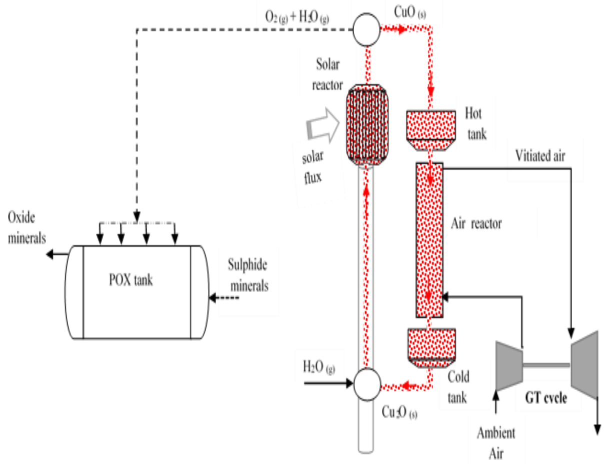

Figure 2. Schematic presentation of coupling a solar chemical looping process with a pressure oxidation process to treat ore sulfides and produce electricity.

To promote the reduction reaction in the solar receiver, steam is used to control the partial pressure of oxygen. The vitiated compressed air in the air reactor is expended in the gas turbine cycle to produce electricity. The O_2/steam mixture is sent to the POX tank where it is used to oxidize ore sulfides.

III. Modeling of the system

In the solar receiver, CuO-particles are reduced to Cu2O using concentrated solar heat through the following endothermic reaction:

$$4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g) \qquad (1)$$

The total solar heat absorbed (Qparticles) by the particles in the solar receiver can be expressed as:

$$Q_{particles} = Q_{sensible} + Q_{chemical} \qquad (2)$$

where: $Q_{chemical}$ is the enthalpy of reaction of Equation (1) and $Q_{sensible}$ is the heat required to raise the temperature of the inlet elements to the reduction temperature.

The heat absorbed by the steam (Qst, red) in the solar receiver can be expressed as:

$$Q_{st,red} = m_{st}(h_{st,red,out} - h_{st,red,in}) \qquad (3)$$

where: ṁ is the mass flow, h is the enthalpy. Subscripts st and rec refer to steam and solar receiver respectively.

The total heat required for the reduction process (Qtotal, red) is the sum of the heat absorbed by the particles and the heat absorbed by the steam.

$$Q_{total,red} = Q_{particles} + Q_{st,red} \qquad (4)$$

In the reactor, Cu2O(s) is oxidized to produce heat, which is used to power the gas turbine combine cycle.

$$2Cu_2O(s) + O_2(g) \rightarrow 4CuO(s) \qquad (5)$$

The work of the gas turbine unit is given by the following expression:

$$W_{GT} = \frac{W_t - W_c}{y_{mec} y_{ele}} \qquad (6)$$

Wt and Wc are respectively the work of the turbine and the compressor. ηmec_ge and ηele_ge are respectively the mechanical and electrical efficiencies of the generator.

The turbine work is:

$$W_t = (m_c - m_{O2\_used})(h_{t,in} - h_{t,out}) \qquad (7)$$

m_c is the air mass flow rate of the compressor, m_{O2}_used is the mass flow rate of the oxygen used in the reactor. h is the enthalpy. Subscrit "in" and "out" refer to the inlet and the outlet of the turbine section.

In the POX, ore sulfides are fed to the POX tank where it is mixed with oxygen, chloride and acid. The ore sulfide is composed of pyrite. It is assumed that the pyrite is completely liberated.

The pressure oxidation process in the POX tank could be represented by the following reactions [13]:

$$O_2(g) \rightarrow O_2(aq) \qquad (8)$$

$$2FeS_2(s) + 7O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{+2}(aq) + 4HSO_4^-(aq) \qquad (9)$$

The intrinsic kinetics of reactions (9) can be described using the shrinking core model for surface reaction control. The respective conversion as functions of oxygen pressure, particle size, and time are given by the following expression [13].

$$x = 1 - [1 - 75.10^6 \frac{P_{O2}}{d_0}. t. \exp(-\frac{13283}{T})]^3 \qquad (10)$$

where: Po2 is the oxygen pressure and it is expressed in atmospheres. do in the diameter of the particles of ore sulfide and it is expressed in centimeters. t is the time in minutes. T is the temperature in C°.

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IV. Results and discussion

Table 1 illustrated the technical data of the POX. The total pressure of the POX tank is the sum of the partial pressure of vapor and the partial pressure of oxygen. The saturation pressure of vapor at 190°C is 12.55 bars.

Therefore, the nominal partial pressure of oxygen is 5.45 bars.

Table 1. Technical data of the POX.

Data	Unit	Value
Average diameter of the particles	Cm	8e-3
Nominal working pressure of the POX	atm	18
Nominal working temperature of the POX	°C	190
Mean time of the particles in the POX tank	Minutes	30

Figure 3 illustrates the effect of the oxygen pressure on the conversion of pyrite. The conversion increases with the increase in oxygen pressure. The higher the oxygen pressure the higher is the amount of oxygen that is required to operate the POX tank. The conversion of pyrite varies from 0.28 to 0.99 for oxygen pressure in the range of 1 to 9 atm. The nominal conversion is 0.859 (oxygen pressure equals to 5.45 bars).

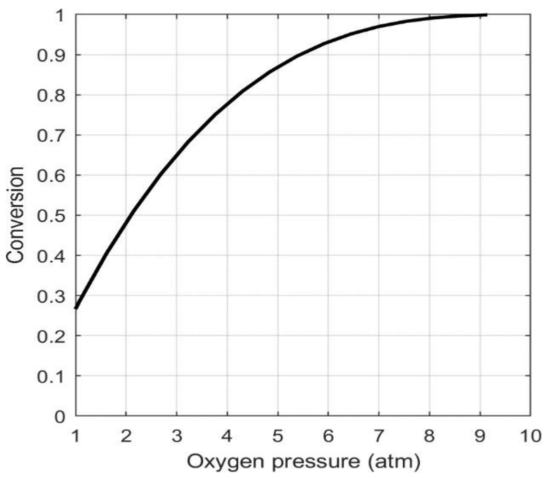

Figure 3. Variation of the conversion of pyrite as a function of oxygen pressure.

The design of the solar particles loop should meet the requirements of the POX tank. In this study, the first objective of coupling the SCL with the POX is to treat ore sulfides so electricity is a by-product. Therefore, it is important to maximize oxygen production.

Figure 4 shows the variation of the heat fraction used to generate oxygen as a function of the cold tank temperature. The higher the temperature of the cold tank the higher is the fraction of the heat used to produce oxygen. Eighty percent of the useful heat of the solar receiver can be used to generate oxygen while the remaining amount can be converted in electricity.

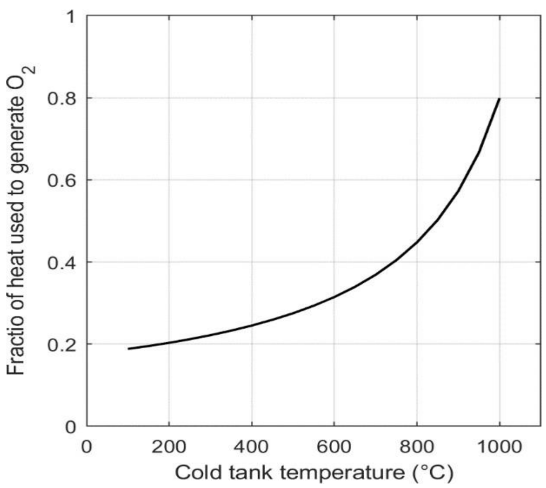

Figure 4. Variation of the useful heat fraction with the cold tank temperature

Assuming that the SCL-POX is designed to treat 10,000 Kg per day of pyrite and it works at steady state. The nominal operating parameters of the SCL are illustrated in Table 2. The molar flow rate of pyrite in the POX tank is 58 moles per minute and the required molar flowrate of oxygen is 202.6 moles per minute.

Table 2. Nominal operating parameters of the SCL.

Data	Unit	Value
Temperature of the solar receiver	°C	1000
Reduction conversion	-	0.5
Oxygen concentration in the solar receiver	-	0.09
Mass fraction of CuO/MgAl2O4	%	60/40
Reduction temperature	°C	1000
Reaction temperature	°C	1000

Figure 5 illustrates the variation of the receiver useful heat and the gas turbine output as a function of the cold tank temperature. The isentropic efficiency of the compressor and the turbine is 0.89 and 0.91 respectively. The ambient air temperature is 25°C. As can be seen, the increase in the cold tank temperature results in a sharp decrease in the receiver useful heat. This reduce the investment costs since the size of the receiver and the heliostat field strongly depend on the useful heat of the receiver. For the considered case, the useful heat of the solar receiver is 3.7 MWth when the cold tank temperature is set at 100°C.

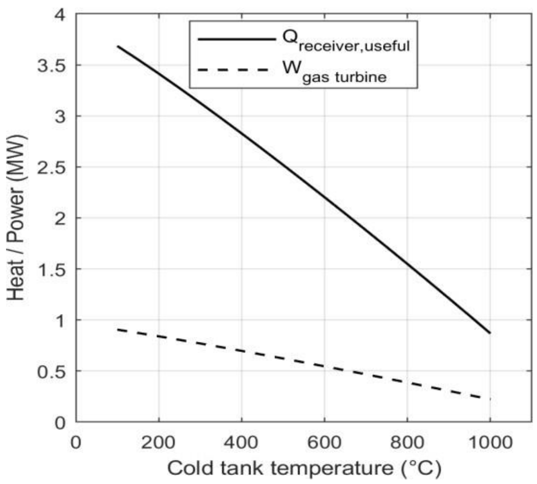

Figure 3. Variation of useful heat of the receiver and the power production as a function of the cold tank temperature

The corresponding electricity production is about 0.9 MWe. If the cold tank temperature is set at 400°C, the required useful solar heat is about 3.1 MWth and the nominal output of the gas turbine is 0.56 MWe. Overall, the higher the cold tank temperature the smaller is the size of the solar receiver and the gas turbine. When the target is the production of oxide minerals, then high temperature is favorable for the cold tank. This offers several advantages including high oxygen production (high production of the oxide minerals in the POX) and low CAPEX because the solar particles loop, the gas turbine and the heliostat field are small.

CONCLUSION

The present paper investigates the integration of a solar thermos-chemical process with pressure oxidation process (SCL-POX) to treat ore sulfides and produce electricity.

A case study to treat 10,000 Kg per day of pyrite is considered and the effect of the temperature of the cold storage tank on the design of the complete system is investigated. The analysis showed that the useful heat of the solar receiver is 3.7 MW_{th} when the cold tank temperature is set at 100°C. However, if the cold tank temperature is set at 400°C, the required useful solar heat is about 3.1 MW_{th}. This means that the temperature of the cold tank has a strong influence on the performance of the SCL-POX.

The proposed SCL-POX is modular and can be adjusted to meet given objectives. It can be adjusted to produce electricity and oxide minerals by adjusting the temperature of the cold tank. When the primary objective is to treat ore sulfides, the temperature of the cold storage tank should be as high as that of the reduction reaction. The proposed system has the potential to store energy and oxygen in a sustainable manner, which offers a great opportunity to overcome the issue of current commercial technologies including low operating temperature of molten salt solar tower technology and the inconvenient of current commercial smelters.

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