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Process simulation and environmental footprint of gold chlorination and cyanidation processes

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Abstract

Chlorination was applied widely in gold processing throughout the 1800s as vat and barrel leaching, with chlorine gas acting as an oxidant. In the early 1900s, hydrometallurgical gold process technology changed from chlorination to cyanidation, which replaced chlorination as the predominant gold leaching process due to technical and financial advantages. The challenges in the chlorination process were related to the highly corrosive leaching chemicals and associated high reagent consumption. In the past, new gold extraction technologies have not been evaluated by their environmental footprint, but rather by the financial, technological and operational advantages. In order to determine the associated ecological impact and sustainability, new transformative technologies need to be evaluated from the environmental footprint point of view prior commercialization. In this study, the environmental indicator category chosen for evaluation was global warming potential (GWP) and the other impact categories, such as human toxicity potential and acidification were left out of the scope. The global warming potentials (GWP) were determined both for the historical chlorination process and for a state-of-art cyanidation process by modelling with HSC Chemistry 8.0 HSC-Sim module combined with life cycle analysis by GaBi 6.0. This analysis provides a baseline scenario for comparison, which can be used to support the future life cycle assessment research for development stage gold processes. The combination of HSC-Sim and GaBi was shown to be an efficient way for the investigation of the environmental footprint of the historical and current gold processes. The GWP of the cyanidation process was 455 kg CO₂ equivalent and the GWP of chlorination process was 10500 kg CO₂ equivalent. The main emission source in cyanidation was found to be electricity, whereas in chlorination the main emissions originated from the chlorine gas, although, it is worth noting that environmental impacts are not defined for all chemical products in the GaBi database. Additionally, some compromises had to be made when the LCA Equivalents were applied to the process streams modelled in HSC-Sim. The corresponding or most appropriate LCA Equivalents were defined from the HSC/GaBi database and the LCA group was defined for all the inputs and outputs within the scope of the process.
Introduction

Traditionally, the financial, technological and operational advantages of the gold extraction technologies have been evaluated, but the focus has not been on the environmental footprint of the process. Nowadays, with the trend toward more restrictive environmental legislation, there is an essential need for research to assess the environmental impacts of existing and development stage gold leaching processes. In this study, the global warming potentials (GWP) of the historical gold chlorination and a state-of-art cyanidation processes were estimated. This information of historical and current industrial processes is needed in order to evaluate the future environmental impacts of new cyanide-free processes.

Life cycle assessment (LCA) is used to make an evaluation of the environmental impact of the product during its lifetime. Life cycle analysis (LCA) is defined by two standards, ISO 14040 [1] and ISO 14044 [2], which belong to the ISO 14000 standard family. In the standards the LCA analysis is divided into four steps, which are:

(i) goal and scope definition phase,
(ii) inventory analysis phase,
(iii) impact assessment phase and
(iv) the interpretation phase.

LCA has been used previously to describe the environmental footprint of gold processes by Li et al. [3]. The emissions to air are usually described as global warming potential (GWP), which is a common impact category used in LCAs. GWP is used to present an estimate of the amount of heat that greenhouse gases trap in the atmosphere in a universal way. The amount of heat trapped by a certain mass of the gas in question is compared to the amount of heat trapped by similar mass of carbon dioxide and the GWP value is presented as a factor of carbon dioxide. Usually, GWP is calculated over a specific time horizon, for example 100 years, with a high GWP value indicating a long atmospheric lifetime and a large infrared absorption.

Life cycle assessment (LCA) has been applied in various environmental impact assessments of metallurgical processes, for example, Rocchetti et al. [4] utilized GaBi software [5] to perform an LCA of the hydrometallurgical processes used for metal recovery from WEEE residues. They studied abiotic depletion, acidification potential, eutrophication potential, global warming potential, ozone layer depletion potential and photochemical ozone creation potential. LCA has also been used to estimate the environmental impact of a bio-hydrometallurgical method for the recycling of spent Zn-Mn batteries in a small pilot experiment [6]. Moreover, Norgate [7] and Molinare [8] have analyzed the sustainability of copper extraction and processing by LCA methods. Norgate [7] and Molinare [8] considered both hydrometallurgical and pyrometallurgical processes. In addition to GWP impacts of each process, Norgate [7] studied acidification potential, and total energy consumption of the processes, whereas Molinare [8] studied terrestrial acidification and other impact indicators for the combined production of 1 tonne of pyrometallurgical and hydrometallurgical copper cathodes.
Although, LCA has been applied widely for the analysis of metallurgical processes, Reuter [9] has already discussed the challenges caused by the use of simplified process routes for metals processing as far back as 1998. He proposed a simulation structure for performing inventory analyses that provides detailed data and gives a solid basis for execution of the ISO 14000 norm and the associated LCA methodology on an industrial ecosystem basis [9].

In this work, the target was to use process simulation software, HSC Chemistry 8.0 [10], and life cycle analysis software, GaBi [5] to assess the environmental impacts of historical and current state-of-art hydrometallurgical gold processes as a gate to gate assessment of LCA. HSC Chemistry is a thermodynamical modelling program and its simulation module, HSC-Sim, can be used to build flowsheets and model the performance of a process. A generic process used in the design of chemical and metallurgical processes includes a steady-state process simulation [11] and the HSC-Sim module is compatible with GaBi software.

Additionally, this study assesses the suitability of the combined use of these programs to determine the global warming potentials (GWP) for gold chlorination and cyanidation processes. First, the processes were modelled in HSC-Sim module for free-milling gold ore, then the simulation data was transferred to GaBi to determine the GWP of the processes. The studied case of chlorination comprised of barrel leaching of free milling gold ore followed by ferrous sulfate precipitation of gold. In contrast, the cyanidation process consisted of cyanide leaching of free milling gold ore and recovery of gold by carbon in pulp and electrowinning. In the next phase of this research, also applicability of the proposed detailed simulation of interconnected material cycles in cyanidation and chlorination environmental footprint analysis will be investigated.

Chlorination process

Chlorination was the major gold leaching process during the 1800s and was first proposed by Dr. John Percy in 1848. At that time, industrial chlorination processes were carried out either as vat leaching or as a barrel process. [12] The vat leaching process is also known as the Plattner process, named after Prof. C.F. Plattner, who applied chlorine gas to the assay of the Reichenstein ores and proposed that a similar method should be applied in larger scale [12, 13]. The barrel process was patented by De Lacy in 1864. Based on De Lacy patent, Dr. Howeel Mears patented another barrel process in 1877 and the Mears process was adapted for use in several mines within the USA.

In the chlorination process, roasted ore or free-milling ore was charged in the barrel with water to create an easily flowing pulp. Chlorine gas was forced into the air-tight barrel under pressure and the barrel was revolved until all gold was dissolved. The barrel was then filled with water in order to discharge the slurry, by gravity, to a leaching vat, where the soluble gold was washed and precipitated. Later Mr. A. Thies made significant improvements to Mears process when it was discovered that chlorine gas could be generated inside the barrel (“in-situ”) to any required extent by the use of bleaching powder (Ca(OCl)2+CaCl2) and sulfuric acid. [12]
In barrel leaching the barrel is revolved at a rate of six to ten revolutions per minute and chlorine gas is introduced into the vessel oxidizing the ore and dissolving gold as chloride complexes [12]. According to Kirke Rose [12] water is added into the barrel first, with roasted pyrites absorbing significantly more water than siliceous ores, usually from 40 to 60%. The chlorine gas is then produced either by dissolving MnO in hydrochloric acid or by generating chlorine gas in situ by adding bleaching powder with dilute acid solution [12]. Gold leaching performed in vats or barrels was described by Kirke Rose [12] with Equation (1) forming gold trichlorid:

\[ 2Au + 3Cl_2 = 2AuCl_3 \]  

(1)

In the chlorination process, chloride for gold complexation originates from the chloride gas (Equation 2). The cathodic reaction can be described as presented in Equation (2). According to thermodynamical observations [13], AuCl₄⁻ is suggested to be the prevailing complex at higher redox potentials whereas AuCl₂⁻ is suggested to be the prevailing complex at lower potentials. Thus the formation of gold chloride complexes according to anodic reactions presented in Equations (3) and (4) can occur in chlorination process. However, the redox potentials are high since chlorine gas is used as an oxidant in chlorination. It can be suggested that gold dissolves as Au(III) form.

\[
\begin{align*}
\text{Cl}_2 \text{(aq)} + 2e^- & \rightarrow 2 \text{Cl}^- & \text{(2)} \\
\text{Au} + 4 \text{Cl}^- & \rightarrow \text{AuCl}_4^- + 3e^- & \text{(3)} \\
\text{Au} + 2 \text{Cl}^- & \rightarrow \text{AuCl}_2^- + e^- & \text{(4)}
\end{align*}
\]

Additionally, a small amount of the chlorine gas can form free hydrochloric acid with water:

\[ 4 \text{Cl}_2 + 4 \text{H}_2\text{O} = 8 \text{HCl} + 2 \text{O}_2 \]  

(5)

The chlorine gas is also known to attack any sulfide minerals present. Sulfide such as iron sulfides are oxidized during chlorination, consuming chlorine gas, Equation (6),

\[ \text{R}_2\text{S} + 4 \text{Cl}_2 + 4 \text{H}_2\text{O} = \text{R}_2\text{SO}_4 + 8 \text{HCl} \]  

(6)

where \( \text{R} \) is the iron compound in sulfide mineral.

In the chlorination process, gold was most commonly recovered from the solution by ferrous sulfate precipitation. Other precipitation methods used included soluble organic compounds, \( \text{H}_2\text{S} \) gas, insoluble sulfides, metals or charcoal. Ferrous sulfate precipitation was favoured in small mills, although this method tended to suffer from slow settling properties and difficulties in filtering. In larger mills hydrogen sulfide was also used, though this method tended to display selectivity issues during the precipitation process. Ferrous sulfate solution was, in most cases, added straight to the gold solution, [12] and the suggested chemical reaction is outlined in Equation (6):

\[ 2 \text{AuCl}_3 + 6 \text{FeSO}_4 = \text{Au}_2 + 2\text{Fe}_3\text{Cl}_6 + 2\text{Fe}_2(\text{SO}_4)_3 \]  

(6)

Although a stoichiometric amount of sulfate was observed as being insufficient for complete gold precipitation, the solid liquid separation of gold precipitate was conducted by settling. Gold was shown to settle better if the solution was well stirred and had free sulfuric acid present, hence sulfuric acid addition and more vigorous stirring was used for up to two hour after precipitation. [12]
Ferrous sulfate was shown to also precipitate other metals like bismuth, lead, calcium, strontium and barium. The formation of basic iron salts could be avoided by use of sulfuric acid, however, if basic iron salts did precipitate, they could be removed with acid or by sagging them off in the furnace. The final gold product was produced by smelting. [12]

**Cyanidation process**

Cyanidation replaced chlorination as the predominant leaching process in the early 1900s due to the comparative technical improvements and financial advantages [14]. The cyanide-gold complex is known to be more stable than chloride-gold complexes, which had in part an effect on the remarkable success of cyanide as lixiviant. [15] The stability of the gold cyanide complex is 38.3, whereas stability of gold chloride complex $\text{AuCl}^-$ is 25.3 and of complex $\text{AuCl}_2^-$ is 9.1. [16] In cyanidation, gold is oxidized with oxygen and a cyanide-gold complex is formed [17].

Since the 1970s, cyanidation has been the dominant industrial gold leaching process and is generally represented by the Elsener Equation (7):

$$4 \text{ Au} + 8 \text{ NaCN} + \text{O}_2 = 4 \text{ NaAu(CN)}_2 + 4 \text{ NaOH} \quad (7)$$

Gold can then recovered by a number of methods including: activated carbon, carbon in pulp (CIP) or in carbon by leaching (CIL) methods, corresponding resin methods (RIP, RIL) or by Merrill-Crowe i.e. zinc precipitation [17]. After precipitation, gold is then deposited at the cathode during the gold electrowinning process according Equation (8):

$$\text{Au(CN)}_2^- + \text{e}^- = \text{Au} + 2 \text{ CN}^- \quad (8)$$

Cyanide leaching is an alkaline process that is conducted in stages, with the optimum pH around 10 to 11. Lime is used for the pH adjustment as $\text{Ca(OH)}_2$ is the cheapest neutralization reagent and can be produced from limestone. The $\text{Ca(OH)}_2$ concentrations added are generally in the range of 0.15-0.25 g/L, which corresponds to lime consumptions of 0.15 – 0.5 kg/t.

Generally, in the industrial processes outlined by Marsden and House [13] the cyanide concentration added to the leaching tank is typically 0.05 to 0.5 g/L NaCN and in agitated cyanide leaching typical cyanide consumptions are 0.25 – 0.75 kg/t of ore. [13]

Copper is known to increase the cyanide and oxygen consumption [18]. Ores that are considered uneconomical to be treated in cyanidation process contain minimum of 0.5 % reactive copper [19] although the present of carbonaceous or sulfide minerals in the ore, kerosene and/or lead nitrate can be used to mitigate the effect on gold dissolution. The optimal lead nitrate addition has to be determined according to the mineralogical composition of the ore and depending on the ore pre-leaching with lead nitrate may be required. Lead nitrate additions of 50 g/ton of ore or 100 g/ton of ore have been investigated previously. [20]

In the cyanidation process model, the ore is first fed into an agitated reactor before the dissolved gold is recovered by activated carbon and re-leached into cyanide solution. The final gold product is
produced by electrowinning and the Detox unit, the cyanide solution is treated by sulfur dioxide/air detoxification [21]. The detoxification reaction is presented in Equation (9)

\[ \text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} + \text{CN}^- = \text{CNO}^- + \text{H}_2\text{SO}_4 \]  

(9)

Materials and Methods

In this study the process models are constructed with HSC-Sim 8.0 and the environmental impact analysis is conducted with GaBi 6.0 software. The aim is to evaluate the environmental impacts of two distinct hydrometallurgical gold processes with this software combination. The purpose of this work is to determine the environmental footprint in terms of GWP for the historical chlorination process and predominant cyanidation process used today for gold leaching in order to compare these processes. In addition, this information can be used in the future as a benchmark for the future development of cyanide-free gold leaching processes.

Composition construction of free-milling gold ore

A free-milling gold ore was chosen as the process material in the models. The free-milling gold ore composition utilised was based on the published mineralogy of Witwatersrand gold ores, a large gold deposit in South Africa. The Witwatersrand region has been the world’s predominant gold-producing area for the past 130 years [13, 22] and the ores consist of three main types of material, coarse quartz pebble material, carbon seams and pyritic quartzite. Gold can be found in the ore mostly as free gold, but there can also be some gold associated with refractory or carbonaceous materials. In these models however, the gold was determined to be free gold instead of refractory gold with only 1 % of sulfides present. [13, 22] Additionally, it was assumed that copper was not present in the ore.

In the report by de Waal [23] three mineralogical compositions for Witwatersrand ores was outlined, and the synthetic ore composition was determined based on the average values, the sulphide minerals present were determined to consist only of pyrite. In the chlorination process, a sulphide concentration above 1 % makes the process economically challenging due to the increase in operational costs resulting from increased chlorine gas consumption [12], therefore, a lower pyrite and higher quartz amount were used for the defined raw material. (Table 1). However, at the time of the report [23] the gold concentration in the Witwatersrand ores was very high compared to modern-day. Due to this the gold concentration was set to 10 ppm for the process models to be more presentable of the situation nowadays.

The sulfide minerals present were determined to consist only of pyrite. In the chlorination process, a sulfide concentration above 1 % makes the process economically challenging due to the increase in operational costs resulting from increased chlorine gas consumption [12], therefore, a lower pyrite and higher quartz amount were used for the defined raw material.
Table 1: The synthetic mineral composition of the free-milling gold ore used in the modelling, based on the published mineralogy of Witwatersrand gold ores.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineral in HSC-Sim</th>
<th>Amount, m-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>Au</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>7.5 ppm</td>
</tr>
<tr>
<td>Uranium oxide</td>
<td>UO₂</td>
<td>870 ppm</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>87.1</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Mg₅Al₂Si₅O₁₀(OH)₈</td>
<td>9</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂(AlSi₃O₁₀)(OH)₂</td>
<td>2.5</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Al₂Si₃O₁₀(OH)₂</td>
<td>0.1</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO₄</td>
<td>0.1</td>
</tr>
<tr>
<td>Chromite</td>
<td>FeCr₂O₄</td>
<td>0.15</td>
</tr>
<tr>
<td>Titanium oxide</td>
<td>TiO₂</td>
<td>0.1</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>1</td>
</tr>
</tbody>
</table>

Process scope of chlorination and cyanidation process model

Chlorination and cyanidation processes were modelled using HSC Chemistry 8.0 software. The chlorination model consisted of three units: barrel leaching, washing and ferrous sulphate precipitation. In contrast, the modelled cyanidation process consists of pre-aeration, leaching, CIP and gold electrowinning. In addition to these processes, sulfur dioxide/air detoxification was also modelled. The studied chlorination process is presented in figure 2, where the dash line box shows the system boundary of the modelled chlorination process. The cyanidation process scope includes more unit processes such as carbon regeneration and detoxification by sulfur dioxide / air. Chlorination process on the other hand is simpler as a historical process. In chlorination process the product is precipitated gold, which is treated by smelting whereas in cyanidation the gold cathodes are the product.
Figure 1: The schematic flowsheet of gold cyanidation process modelled in this study. The scope of the modelled cyanidation process includes all stages presented.

Figure 2: The schematic flowsheet of gold chlorination process. The dash line box shows the scope of the modelled chlorination process.
Process design parameters

The design parameters for process models constructed in HSC-Sim were formulated based on the available literature, estimation of parameters and HSC-Sim calculations. The process design parameters used are shown in Table 2.

The process models in HSC-Sim were constructed based on design parameters presented in Table 2 and the reactions outlined previously (Equations 1 – 6). The design parameter values were formulated based on the existing literature, estimation of parameters and HSC-Sim calculations. The feed rate of free-milling gold ore was determined as 150 t/h for both processes. This feed rate corresponds to a gold production of 345 600 ounces of gold/year when gold concentration in the ore is 10 ppm and 90 % of the gold is recovered.

The solid liquid ratio of the chlorination process was selected to be 50 wt.-% to produce an easily flowing pulp [12]. For the cyanidation process model the solid liquid concentration in the preaeration tank was determined to be 300 g/L. The cyanide solution, thickened slurry and lime are all mixed together in the preaeration tank with an optimum pH is around 10 to 11 [13]. In the model the Ca(OH)\textsubscript{2} input concentration was set to 20 % to give a pH value 11 and the cyanide solution concentration was set to 20 %.

The chlorine gas input modelled was set to be equal to the amount of chlorine used in the reactions, with the efficiency of chlorine gas of 60 %. The progress of gold oxidation was determined as 90 %, and the progress of sulfide mineral dissolution 80 %. In cyanidation, oxygen – which oxidizes gold – is usually introduced via as air purged into the leaching solution. Oxygen concentration can be maintained at or even slightly above calculated saturation levels with air purging and this principle was applied in the model. Lime, Ca(OH)\textsubscript{2}, is added separately in this tank to make sure that the pH is maintained at 11. The progress of gold dissolution is set to 95 % and the progress of silver dissolution to 65 % with further, about 2% of the pyrite present also set to react.

In the chlorination process, the solution is filtrated out of the barrel after leaching and directed into the gold precipitation unit. The leach residue is then washed and the wash water partially directed to precipitation unit. The input washing water amount used in the barrel process was set to 0.5 m\textsuperscript{3}/t solids and the cake moisture was estimated as 18 % after the leach residue washing. To imitate the historical chlorination process, the washing efficiency was determined to be as low as 70 % and according to this value the feed solution in cake is 5.4 %. The feed solution in cake is calculated according to Equation (10),

\[
\text{Feed solution in cake} = \frac{\text{Filter cake moisture} }{ (100 - \text{washing efficiency}) / 100}
\]

(10)
Table 2: The process design parameters used in the HSC-Sim modelling.

<table>
<thead>
<tr>
<th>Design parameters</th>
<th>Chlorination</th>
<th>Cyanidation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total amount of the ore in Witwatersrand area</td>
<td>150 t/h</td>
<td>150 t/h</td>
<td>Estimation</td>
</tr>
<tr>
<td>Retention time in barrel/reactor</td>
<td>1.5 – 2 h</td>
<td>Total 20 – 40 h, 6 – 12 h per reactor</td>
<td>[12, 11]</td>
</tr>
<tr>
<td>s/l ratio</td>
<td>50 wt.-%</td>
<td>300 g/L</td>
<td>Estimate based on [12]</td>
</tr>
<tr>
<td>Cl₂ / O₂ consumption</td>
<td>Stoichiometrical with 60 % efficiency in Au leaching</td>
<td>at or even slightly above calculated saturation levels</td>
<td>[13]</td>
</tr>
<tr>
<td>Filtration washing efficiency</td>
<td>70 %</td>
<td></td>
<td>Estimate</td>
</tr>
<tr>
<td>Cake moisture</td>
<td>18 %</td>
<td></td>
<td>Estimate</td>
</tr>
<tr>
<td>Washing water needed for ton solids</td>
<td>0.5 m³/t</td>
<td></td>
<td>Estimate</td>
</tr>
<tr>
<td>FeSO₄ input</td>
<td>0.028 t/h</td>
<td></td>
<td>Stoichiometrical multiplied by 10</td>
</tr>
<tr>
<td>Lime concentration</td>
<td>0.15 – 0.25 g/L or 20 %</td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>Cyanide concentration</td>
<td>0.05 to 0.5 g/L or 20 %</td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>Gold concentration in EW</td>
<td>1 g/L</td>
<td></td>
<td>Estimated based on [24]</td>
</tr>
<tr>
<td>Hydrochloric acid concentration in carbon washing</td>
<td>20 % (pH 2)</td>
<td></td>
<td>Estimate</td>
</tr>
<tr>
<td>SO₂ input</td>
<td>0.03 t/h</td>
<td></td>
<td>Stoichiometrical [3, 13]</td>
</tr>
<tr>
<td>Electricity</td>
<td>945 kWh</td>
<td>458 kWh</td>
<td>Chlorination based on the agitator energy required</td>
</tr>
<tr>
<td>Gold oxidation progress</td>
<td>90 %</td>
<td>95 %</td>
<td>Estimated</td>
</tr>
<tr>
<td>Sulfide mineral oxidation progress</td>
<td>80 %</td>
<td>2 %</td>
<td>Estimated</td>
</tr>
<tr>
<td>Silver oxidation progress</td>
<td>Not included</td>
<td>65 %</td>
<td>Estimated</td>
</tr>
<tr>
<td>Gold absorption to activated carbon progress</td>
<td>95 %</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>Silver absorption to activated carbon progress</td>
<td>95 %</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>Activated carbon input</td>
<td>480 t/gold ton</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>Gold reaction progress in Electrowinning</td>
<td>99 %</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>Silver reaction progress in Electrowinning</td>
<td>99 %</td>
<td></td>
<td>Estimated</td>
</tr>
</tbody>
</table>
The final step in the chlorination process is ferrous sulfate precipitation. In the precipitation unit, gold is precipitated from the filtrate and wash water solutions. In the HSC-Sim model, the amount of FeSO₄ was controlled by the amount required in the precipitation reactions, which was multiplied by 10 according to the fact that stoichiometric amount is deemed to be insufficient. The gold precipitation reaction progress was determined as 90%. The gold extraction in the simulation model was 82.6%, whereas the silver dissolution was not modelled in this case.

In the cyanidation process model carbon in pulp (CIP) was used for the gold recovery. Progress of gold and silver absorption reactions on the activated carbon is 95% and the input of activated carbon was set to be 480 t/gold ton. The activated carbon loaded with gold is screened and directed to carbon elution. In carbon elution, fresh cyanide solution is charged in along with water and the cyanide concentration was set to be 2 g/L in the output solution to electrowinning. The carbon is recycled back to the CIP unit. In the carbon regeneration carbon is washed with hydrochloric acid, where the solution pH is set to be 2.

The gold is recovered from the concentrated cyanide solution by electrowinning. The recovery of gold and silver electrowinning is 99%. The gold concentration for electrowinning is 1 g/L [24] and the cyanide concentration in the electrowinning solution is 2 g/L. The recovery of gold in cyanidation simulation was 91.3% and the silver recovery was 60.7%.

Furthermore, the treatment of wastes was partially modelled in the cyanidation process. After leaching the slurry is thickened. The overflow of the thickener is partially directed back to leaching in order to keep the desired s/l ratio (300 g/L) in the leaching unit, where also chemical concentrations are adjusted. The bleed solution is treated in the Detox unit by the sulfur dioxide/air method. In the Detox unit the cyanide solution is transferred to cyanate, OCN⁻ form by SO₂ and O₂. The SO₂ and air ratio was estimated as 90% of air and 10% of sulfur dioxide and calculated according to the SO₂ amount used in the reactions. The solution can then be directed into a pond, deep sea or other method, depending on local regulations.

Electricity consumption estimation is not included in the HSC-Sim module, therefore, the electricity consumption of the historical barrel process was assessed in this study by estimating the energy needed for the agitation of barrel with the state-of-art equipment. The residence time in barrel leaching was about 1.5 – 2 hours [12] and in the Thies process about 6 hours. A residence time of 2 hours was used in the model calculations and the amount of electricity required was defined by determining the effective volume (209 m³) of the barrel based on raw material feed and S/L ratio used. According to these values, approximately 3 reactors are needed to treat the input feed amount of this process. Based on the defined reactor volume, the agitator diameter was calculated to be 2.9 m. The power number of the reactor was 3.5 and the tip speed 5.5. The agitator speed was calculated from the tip speed following Equation (11):

\[ \omega_T = \pi D N \]  

(11)

where \( \omega_T \) is tip speed, \( D \) is diameter of the agitator and the \( N \) is the agitator speed 1/s.
The absorbed power to slurry was calculated using Equation (12),
\[ P = N_P \cdot \rho \cdot N^3 \cdot D^5 \]  
(12)
where \( N_P \) is the power number, \( \rho \) is the density, \( N \) is the agitator speed and \( D \) is the impeller diameter. The power losses and safety factors are taken account by increasing the minimum required electric power by 20%. The minimum required electric motor power was in this case estimated as 290 kW. Based on these values, a motor to provide the needed energy for the agitation would require 315 kWh electricity and as there would be 3 reactors, the electricity amount needed would be three times 315 kWh, corresponding to 945 kWh.

Previously, for cyanidation, air agitated leaching tanks were used in the industry, but mechanically agitated reactors have gained preference due to their lower operating costs. Depending on the nature of the ore and the number of leaching tanks in series, the residence time of the ore in the leaching process is in the range of 20 to 40 hours [11]. This means that the residence time in one reactor varies between 6 to 12 hours. This information can be used in equipment design to determine the electricity consumption, however, in this study the electricity consumptions in the cyanidation process model was determined according to the LCA analysis of Li et al. [3]. The cyanide leaching and CIP recovery process need 3.52 x 10^6 kWh/ of electricity per 1 tonne of gold, corresponding to 457 kWh in the modelled cyanide process. The gold electrowinning process is known to require 112 kWh/per 1 tonne gold produced [13]. This equates to a total electricity requirement of 458 kWh for the modelled process.

Results

The environmental footprint of cyanidation and chlorination processes was investigated in terms of global warming potential (GWP). The environmental footprint was calculated with GaBi 6.0 software and the calculations were made based on the HSC-Sim model with estimations of the process equipment electricity consumption. The LCA tool in the HSC-Sim module was used to conduct the first two phases of life cycle assessment,
(i) goal and scope and
(ii) life cycle inventory.

The corresponding or best approximate LCA equivalents were determined from the HSC/GaBi database and the correct LCA group was defined for the inputs and outputs. The functional unit, which is the quantified performance of a product system for use as a reference unit, is 1 kg of gold. The input and output values were normalized to produce 1 kg of gold and the simulated process data with the LCA inventory analysis was transferred to GaBi 6.0 software. The main interest in this study was to calculate global warming potential (GWP) over a 100 year time interval for both the chlorination and cyanidation processes. It was found out that the LCA analysis accuracy depends on the corresponding Equivalents that are found in the GaBi database. For that reason, the conducted LCA analysis can be suggested to give some indication of the process environmental impacts, but it
is only representative due to the database limitations. The GWP values for chlorination process are presented in Figure 3. The main emission in this process is the chlorine gas production as the environmental impact of ferrous sulfate, FeSO₄, is not taken into account due to the absence of appropriate data in the GaBi database. The results of GaBi analysis for cyanidation process are presented in Figure 4. The main emission source is the electricity in the process. Due to the fact that production impacts for sodium cyanide were not available in the GaBi database, this input is not taken into account in GWP calculation. Additionally, the production emissions of 20 % hydrochloric acid was not found in GaBi, so the production emissions of 32 % hydrochloric acid was used as a reasonable estimate.

Figure 3: The total and process specific GWP values of the chlorination process modelled in the HSC-Sim module. GWP per 1 kg of Au (over 100 years) values were calculated with GaBi 6.0.
Figure 4: The total and process specific GWP values of the cyanidation process modelled in the HSC-Sim module. GWP per 1 kg of Au (over 100 years) values were calculated with GaBi 6.0.

From Figure 3 and Figure 4 can be seen that the environmental impact in the form of GWP is much higher in the chlorination process. This is mainly due to the fact that the chlorine gas production results in large emissions to the surrounding atmosphere. Chlorine gas production was not modelled in the HSC-Sim, and a most suitable chlorine gas production was chosen from GaBi database. In the process chosen from GaBi chlorine gas is produced in the electrowinning process. This is different when compared to the method used in the 1800s to produce chlorine gas and has a great impact on the LCA results of chlorination process. However, the initial comparison of the historical and state-of-art gold technologies by their environmental impact shows that the technological change that took place at the turn of 1900’s was advantageous as GWP lowers remarkably with the decrease in Cl2 gas usage. Again this suggests that the new development stage chloride process show promise, when the usage of chlorination gas is not applied. Instead chlorine ions are supplied in these processes as salts, which could suggest lower GWP values for the development stage i.e. as Nippon N-Chlo [25] HydroCopper [26], Outotec Gold Chloride process [27], Dundee [28,29], Intec [30], Platsol [31], and Neomet [32].
Conclusions

This study presents the process models of chlorination and cyanidation processes for historically used free-milling gold ore. The aim of this study was to investigate of the environmental impact of historical and current hydrometallurgical gold processes by HSC-Sim 8.0 and GaBi 6.0. It was found out that the determination of the outputs and inputs for the LCA analysis was incomplete due to lack of certain chemicals such as FeSO₄ and NaCN in the database. Nevertheless, HSC-Sim modelling combined with GaBi life cycle analysis can be an efficient tool to estimate the emissions of hydrometallurgical processes for current and developmental stage hydrometallurgical processes.

The environmental impact indicator investigated in this study was GWP. However, there are more environmental indicators, which will be later investigated in more detail. The total GWP of the modelled cyanidation process was calculated with GaBi software to be a 455 kg CO₂ equivalent, with the main emission from the electricity needed for process operation. The total GWP of the modelled chlorination process was 10500 kg CO₂ equivalent, and in this historical process the main emission source was shown to be chlorine gas production.

These results suggest that the technological transformation in the early 1900’s resulted in a positive environmental impact as the cyanidation took over chlorination technology although, the GWP calculated is in this stage of modelling is only indicative due to insufficient data in the LCA software.

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