Sustainable and energy efficient leaching of tungsten (W) by ultrasound controlled cavitation

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The project was funded by SIP-Strim and implemented in parallel with an ERA-MIN project funded by Vinnova. The project is a collaboration between the research subject areas of Engineering Acoustics and Process Metallurgy at the Luleå University of Technology. The project leader Örjan Johansson is also the principle expert in acoustic optimization. The expertise in Hydrometallurgy was secured by Professor Åke Sandström and Dr Mohammad Khoshkhoo. Laboratory support for the leaching experiments were given by Jane Mulenshi and Britt-Louise Holmqvist. Finally, the numerical modeling and acoustic optimization conducted by Taraka Pamidi.

The current project is within the field of hydro-metallurgy with the aim to increase both metal recoveries and energy efficiencies in leaching processes. Target materials to be treated in the project include elements listed by the European Commission in their list of Critical Raw Materials where tungsten is an example. The choice to leach Scheelite (CaWO4) is due to its well-known difficulties to be leached.

The project is linked to CAMM (center of advanced mining and metallurgy) at Luleå University of Technology, based on strategic funds from the Swedish government within the strategic area “Sustainable use of natural resources: mining and minerals.” The project also supports sustainable use of raw materials since the project will partly be linked with the ERA-MIN project “REMinE” (Improve Resource Efficiency and Minimize Environmental Footprint) financed by Vinnova where possibilities to extract mineral and metals from historical mine waste will be studied. Boliden Mineral AB will be involved in discussions regarding project planning and outcomes.

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Summary

The project aims to use ultrasound controlled cavitation to achieve a more energy efficient leaching process. Locally, collapsing cavitation bubbles cause an extremely high pressure, shock waves and high temperature, which provide an opportunity to perform the leaching process at a much lower temperature than in an autoclave (20 bar overpressure and 220 °C). The results show that the method works, but that a higher static pressure and thus temperatures are necessary to achieve a leaching recovery rate corresponding to today's autoclave technology. Another process parameter of importance is flow control and the initiation of cavitation bubbles that occur through a geometrically optimized nozzle (orifice plate). Numerical and experimental adaptation of the developed reactor with respect to the leaching conditions (Sodium hydroxide and Scheelite concentrate), required more time than expected. Best test results show that an energy supplement with ultrasonic controlled cavitation of 104 kWh / kg increases the leaching recovery by 21%. The leaching reagent temperature 60° C was determined regarding available reference data and was thought to be close to optimum for intensive cavitation in atmospheric pressure. Optimum temperature relates to the leaching reagent, vaporization temperature, density, boiling point, surface tension, and viscosity. Generally, for leaching is that higher temperatures are required to increase the chemical reaction rate (requires overpressure). The modified reactor principle provides stable results and is possible to scale up. Higher cavitation intensity for shorter finishing time and higher recovery rate require advanced flow induction, multiple excitation frequencies adapted to the optimized reactor geometry, as well as optimal process pressure and temperature.
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1. Aim and Objectives

The project aims to improve the leaching process by utilizing ultrasound cavitation, for the treatment of difficult to leach materials. Ultrasound controlled cavitation is known to give an accelerated leaching process with higher yield, at a lower temperature in comparison to existing technologies. The question is if it would be possible to do this in a more sustainable way. Target material in the project is Scheelite concentrate (CaWO₄) that requires very severe leaching conditions regarding temperature and pressure, i.e. autoclave leaching, and thus becomes energy intensive. The objective is to optimize the process regarding ultrasound intensity, excitation frequency, flow control, temperature and input power using a previously developed cavitation reactor concept.

The reactor principle is based on a two-step cavitation procedure. First cavitation bubbles are initiated through a nozzle and then collapsed by high intensity ultrasound in a resonant chamber. In this stage, the nozzle geometry used for the initiation of cavitation bubbles is not yet optimized. Results of pre-studies have confirmed that the process is highly temperature dependent. To maximize the cavitation intensity, the process temperature must be optimized with regard to static pressure and the boiling temperature of the leaching reagent. However, the reported experimental series is made at normal pressure. Increased static pressure enables higher cavitation intensity.

A limitation in the current experimental setup is that the volume of the cavitation reactor only represents 50% of the total circulating volume. This means that the energy supplied to the material to leached can almost be doubled in an up-scaled reactor geometry (longer tube), thereby doubling the yield for a given exposure time. A longer reactor (vertical orientation) also means a natural increase in the static pressure in the system.

The objective is to fine tune the developed reactor design on various types of Scheelite material and leaching conditions. The project also includes a particular benchmark with alternative technologies energy use. Another goal is also to tie a manufacturer of equipment to the project. By a combination of expertise in acoustic optimization and hydrometallurgy, the ambitious targets for resource and energy efficient leaching can be reached.

The ultimate goal of the project is to establish a new innovative energy efficient leaching method to recover valuable elements from by-products and
concentrates. The project aims to increase the technology readiness level of the current reactor principle for leaching from TRL 3 to TRL 5.

A successful outcome of the new pre-study will give an option to upgrade existing reactor to a larger scale. One aspect is basically a much longer reactor tube, but also to secure that optimal leaching condition is obtained. The up-scaled reactor performance will then be tested and evaluated in a realistic environment (TRL6). This requires an involvement of a sub-contractor able for precision manufacturing of stainless steel tube components, but also a greater involvement of companies like Outotec and Boliden. The final goal is to implement the new technology on a pilot scale level (TRL 7).
2. Theoretical Background

Process intensification by high power ultrasound to generate transient cavitation has a great potential in industrial application. A thorough summary of the situation given in the book 'Power Ultrasonics' [1]. There are several possible applications of ultrasound controlled cavitation within mineral processing and hydrometallurgy. Examples are improved dispersion and mixing of mineral particles in suspension, cleaning, and activation of particle surfaces by cavitation, removal of the diffusion layer around particles and micro-grinding by increasing the particle collision, etc. Separation methods are often described as a kinetic process and show both an increased yield and improved efficiency during ultrasound excitation. Metal extraction by a leaching process can be more efficient with ultrasound assistance due to very high local temperatures (which increase the solubility and diffusivity) and high pressures (which favor penetration and transport) that occur when cavitation bubbles form and collapse close to particle surfaces, see Figure 1. When cavitation occurs in a liquid close to a particle the cavity collapse is asymmetrical and high-speed jets of liquid are produced.

Figure 1. Principle of ultrasound cavitation [16]. The initiated bubbles grow due to evaporation and finally reach critical size (resonant) when it grows quickly and collapse violently.
The impact of these jets on the particle surface is very strong and can after impact produce newly exposed and highly reactive surfaces. Additional effects are so-called secondary flows, known as acoustic streaming, which can remove reaction products from the surfaces and thereby significantly reduce diffusion layers so that the leaching progresses faster[2]. Based on the properties given above ultrasound has the potential to be beneficial in hydrometallurgy by improving both leaching kinetics and recoveries. The following two cases can be identified where ultrasound could improve leaching:

- Leaching of minerals where leaching proceeds through the surface reaction controlled mechanism characterized by a high activation energy. Minerals that fall into this category are tetrahedrite, nickel laterites, scheelite, wolframite, etc., these types of minerals are typically leached in autoclaves at elevated pressures (up to 20 bars) and temperatures (up to 240ºC) making them highly energy intensive. Other examples are metallurgical by-products like slag, dust, etc. where speiss formed in base metal production is one example. The possibility to perform the leaching at lower temperatures under atmospheric pressures has significant energy saving opportunities[3].

- Leaching processes where leaching kinetics are slow due to the formation of diffusion layers forming on the surface of the particles to be leached, i.e. through the diffusion controlled mechanism. This is the case for leaching of chalcopyrite in sulfate solution where the chalcopyrite surface with time is known to be passivated by the formation of a surface layer resulting in low copper recoveries. Another example is during cyanide leaching for gold extraction where the gold particles sometimes get covered by clay or oxide layers. In these cases, ultrasound can remove these layers and give higher metal recoveries during leaching[4].

Despite these generally accepted benefits of ultrasound assisted leaching the method is not practiced in hydrometallurgical processes. This is because that the controlled cavitation is not fully developed and problems are encountered in the implementation on a larger scale. The technology can be unstable, have low energy efficiency, and in some applications, have a short lifespan. On the plus side is that the technology can produce results not achievable otherwise. Identified challenges involve acoustic optimization of a highly-coupled system requires extensive optimization for the specific application. Good results require close collaboration of several different areas of knowledge, which is possible with some of the topics that are represented at the Luleå University of Technology. In contexts where energy costs are high, there is a particular need to optimize the process, which largely applies to a leaching process, in which a reduced energy demand and the faster process is a prerequisite for profitability.

Achieving transient cavitation requires knowledge of how different excitation mechanisms and resonance principles can interact and be optimized [5]–[14]. The reinforcement required can be partially achieved through resonance by geometrical
optimization of the surrounding structure and fluid volume, i.e. excitation frequency is tuned in relation to the wavelength in a defined volume. To achieve a high efficiency of energy transfer from the electrical power to the efficiency of the leaching process, a number of development and optimization steps are needed. The most fundamental aspects are:

- Feeding techniques to initiate cavitation bubbles and to maintain an even distribution of solid mineral particles in the aqueous leaching solution.
- The ultrasonic excitation to create the transient collapse of oscillating cavitation bubbles.
- Optimization and adaptation of a number of interconnected resonant systems.

Experimental analysis of the parameters which affect the leaching process, e.g., chemical and mineralogical composition of the material, type of leaching reagent and its concentration, solid concentration and density of the pulp, mineral particle size distribution and surface area, flow rate, supplied cavitation intensity, temperature, and static pressure.

The problem can be seen as a chain of components and aspects coupled to each other that needs to be optimized for efficient conversion of electrical power to resonance enhanced ultrasound, and finally as mechanical energy on the solid in the leaching reagent. Input electric power is controlled by feedback to the signal generator, via measurement outside the fluid volume (pressure signal's frequency spectrum). Flow and pressure are used as control parameters for creating a stable operating condition, see Figure 2.

Figure 2. Conversion of electrical power into mechanical energy in the form of vibrations and sound waves to excite and collapse cavitation bubbles on the Scheelite emerged in the leaching reagent. Flow conditions and static pressure are control parameters for creating stable and optimum operating conditions.
Figure 3. Principal solution for the developed ultrasound controlled cavitation reactor.

Figure 4. a) Photograph of the reactor adapted for leaching of Scheelite using sodium hydroxide as leaching reagent, b) FE-calculated pressure response seen as a cross section of the reactor, excited at 37 kHz (41 kHz in experimental verification). In reality maximum at a single frequency is 195 dB and the non-linear response is seen as a harmonic spectrum with amplitudes as high as at the excitation frequency.
3. Methods and Procedure

3.1 Material to be leached

The leaching object studied in this project has high activation energy and thus leached with the surface reaction controlled leaching mechanism. The object is a concentrate of Scheelite (CaWO₄), an oxide mineral. In industrial processes Scheelite is leached in autoclaves at temperatures around 200°C in alkali solutions that can be either sodium carbonate or sodium hydroxide. Alkali concentration during leaching is high and thus gives a highly viscous leaching solution. An alternative object of interest would be Speiss formed in the settling furnace during slag treatment in Boliden’s copper smelter at Rönnskär. Speiss is a high-density product consisting of antimonides and arsenides with relatively high concentrations of copper, tin, nickel and precious metals. Speiss is very difficult to treat both through pyrometallurgy and hydrometallurgy. Alkaline sulfide or polysulfide leaching at high temperatures during long leaching time can be used to leach antimony, tin selectively, and arsenic is leaving the base and precious metals in the residue for recovery in separate processes. Thus, in both cases, there is a lot to gain in metal recovery and energy cost if ultrasound controlled cavitation can intensify the leaching process and allowing leaching to be performed at lower temperatures under atmospheric pressure.

3.2 Optimization procedure and experimental design

Energy efficient process intensification can be achieved by a combination of hydrodynamic and ultrasonic controlled cavitation. A key aspect of this project is to experimentally optimize the developed prototype reactor to enable energy efficient leaching. The reactor consists of an adjustable nozzle and a subsequent resonant reactor volume excited by ultrasound at fixed frequencies (Figure 3). The mineral suspension flows through an inner tube in the center of the water-filled reactor. The conceptual reactor solution is developed and optimized by numerical modeling and experimental verification [12-14]. Numerical simulation is made using the commercial available software Comsol Multi Physics.

The design goal is to create maximum pressure variations in the central part of the reactor where the mineral suspension is forced to be. By that cavitation bubbles and clouds of bubbles are collapsed near or on the surface of the particles in the suspension, transferred through the reactor in a separate PVC-plastic tube centered in the cylindrical volume.

Optimum performance of the reactor requires a multivariate tuning procedure. Factors of importance are excitation frequency, concentration, temperature, static pressure, input power, exposure time and flow rate. Minimizing the overall loss factor is a critical aspect for optimal results. Another aspect of importance is to induce cavitation bubbles by flow through a narrow section. In this case a nozzle,
which is a 5 mm thick cylindrical disc with a number of small holes in a geometrical pattern [15]. Up-scaling is possible by extending the reactor tube, and by connection of several tubes in parallel or series. A key aspect for an energy efficient leaching process is to collapse cavitation bubbles proportional to the size of mineral particle structures. The bubble size is related to the excitation frequency. The geometry and structure properties of the reactor are optimized for three different frequencies, 22 kHz, 37 kHz and 53 kHz (Figures 4 and 7). Increasing excitation frequency reduces the size of cavitation bubbles. However, to maximize cavitation intensity a combination of several excitation frequencies is likely to be the best option [10, 11].

The optimization strategy refers to:

- Definition of the linkage between the leaching solution and solid material regarding cavitation intensity, excitation frequency, and flow induced excitation
- Process parameter optimization (temperature, concentration, static pressure, flow) to achieve energy efficient leaching of tungsten (W) from Scheelite concentrate of different size distributions

The planned project was implemented as a parallel process with the objectives shown in Table 1.

**Table 1: Time Plan**

<table>
<thead>
<tr>
<th>Time Plan</th>
<th>Sep-Oct</th>
<th>Nov-Dec</th>
<th>Jan-Feb 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimization of excitation frequency, static pressure, temperature, and process parameters like size distribution of the scheelite concentrate *</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaluate different nozzle geometries for flow induced cavitation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaluation of energy efficiency and up-scaling potential</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reporting and workshops</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Various Scheelite concentrates and leaching conditions to be evaluated regarding kinetics and recoveries.

The project deliverables can be summarized as:

- Optimized process parameters with respect to leaching recovery and kinetics, regard to temperature, excitation frequency, solid concentration, and particle size
- Defined principles for reactor design and upscaling
- Estimated energy efficiency potential in full-scale implementation
3.3 Geometrical dimensions of Tube reactor

Table: Optimization parameters
LWC: Length of water column  
LEP: Length of end plug
ZTS: Distance to Sonotrode position
DT: Outer diameter of tube
HTW: Thickness of tube wall
HS: Total height of Sonotrode
dIT: Diameter of inner tube
hIT: Thickness of inner tube

The tube wall is excited by the Sonotrodes, which consists of a resonant structure and integrated piezo-ceramic elements. Vibration is excited by an electrical signal that varies over time, for example as a pure sin at a fixed and for the reactor's optimum frequency. Optimized and powerful excitation of the reactor walls gives rise to high-efficiency and controllable cavitation intensity that affects the leaching reagent through the inner tube.
The reactor was built as a 3D-model and the mesh on all domains was made up by tetrahedral elements, in total 166924. In order to consider a quasi-static approximation for each elementary triangular element, the segment length should be shorter than approximately $\lambda/5$. This permits a real concession between computational time and precision in the results.

To verify the numerical calculations and to validate the method a number of experiments were performed, see Table 2.

Table 2: Experimental design to verify leaching recovery with ultrasound controlled cavitation

<table>
<thead>
<tr>
<th>Test (Nr)</th>
<th>Ultrasound Frequency (Hz)</th>
<th>Hydrodynamic cavitation</th>
<th>Ultrasound Power (W)</th>
<th>Flowrate (l/min)</th>
<th>Temp ($^\circ$C)</th>
<th>Time (Hours)</th>
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<tbody>
<tr>
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<td>---</td>
<td>No</td>
<td>36.2</td>
<td>0.53</td>
<td>38</td>
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<tr>
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<td>0.53</td>
<td>60</td>
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<tr>
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<td>0.53</td>
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<td>4</td>
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<td>43480</td>
<td>Yes</td>
<td>187 (only f1)</td>
<td>0.53</td>
<td>60</td>
</tr>
</tbody>
</table>
4. Results

Optimization of the ultrasonic reactor geometry design is evaluated with both combination of numerical modeling and experimental verification. The goal of the design is to create high vibration amplitude in the tubewall and a high sound pressure in the center of the water volume. High-pressure zones (sound pressure variation) causes high cavitation intensity. Figure 6 shows the calculated frequency response of the reactor when excited with two frequencies. Calculation is performed with stepwise sine excitation, giving the linear system response at each frequency.

![Graph showing frequency response](image)

*Figure 6. Estimated linear frequency response (calculated stepwise for one frequency at the time) for FE-modeled and optimized cavitation reactor. Pressure response is determined along the central line of the reactor, with a loss factor of 2% (experimentally determined). In the real application, the pressure response to a pure sine become non-linear and the excitation signal become distorted, seen as a harmonic spectrum in frequency domain.*
The ultrasound cavitation reactor was adapted to handle a highly-concentrated leaching reagent (sodium hydroxide, 10M) and a flotation concentrate of Scheelite, a mineral containing tungsten (W). The excitation signal was adapted to the reactor's experimentally optimized frequency response (22.8 kHz or/and 41.3 kHz). Process parameters such as flow, temperature, cavitation intensity and signal frequency was varied. Tests were conducted at 38 and 60 ° C with excitation of 23 kHz and 23 + 41 kHz. The temperature 60° C was selected for comparison with reference data. Flow-induced cavitation was initiated via a specially designed nozzle (orifice plate), see Figure 3.

The pre-studies have shown that the new reactor principle has good potential in improving the recoveries in a leaching process figure 8. The results showed that the ultrasound controlled cavitation accelerated leaching of tungsten (W) from the Scheelite concentrate (40% sodium hydroxide as leaching reagent). Compared with a blank test 21% higher tungsten recovery was obtained after an exposure equivalent to 104 kWh/kg (Table 3 and Figure 8). 23 % recovery of tungsten was achieved after 5 hours. Extrapolation of the results indicates that a recovery of 80 % would be possible within a time frame of 16 hours.
Table 3: Experimental design and leaching recovery with ultrasound controlled cavitation

<table>
<thead>
<tr>
<th>Test (Nr)</th>
<th>Ultrasound Frequency (Hz)</th>
<th>Hydrodynamic cavitation</th>
<th>Ultrasound Power (W)</th>
<th>Temp (°C)</th>
<th>Time (Hours)</th>
<th>Tungsten Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>f1 22899</td>
<td>---</td>
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<td>36.2</td>
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<td>---</td>
<td>No</td>
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<td>60</td>
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<td>187 (only f1)</td>
<td>60</td>
<td>5</td>
<td>19.1 20.4</td>
</tr>
</tbody>
</table>

Figure 8. The result of a 5 hours leaching of Scheelite, intensified by ultrasound Controlled cavitation, in comparison to other methods. The input electrical power was equivalent to 104 kWh/kg Scheelite concentrate.
5. Discussion

An observed limitation of the used methodology was that the volume of the current cavitation reactor only represents 50% of the total exposure volume. This means that the energy supplied to the material to be leached can almost be doubled in an up-scaled reactor geometry (longer tube), thereby doubling the yield for a given exposure time. A higher temperature is also required. The key is to determine the optimum process temperature relative to the boiling temperature of the leaching reagent. The leaching reagent has a boiling temperature of 142 degrees. To reach a higher process temperature the static pressure of the stagnant water volume needs to be increased. However, this will also enable higher cavitation intensity. Finally, there is a need for further development of the nozzle used for the initiation of cavitation bubbles by the flow. An observed problem was that bigger particles of Scheelite concentrate got trapped and did not go through the ultrasound reactor.

The objective with the ongoing project is to fine tune the developed reactor design with respect to various types of Scheelite material and leaching conditions. A special focus will be on tuning the flow induced cavitation and optimum process temperature. The project will also include a careful benchmark with alternative technologies energy use. Another goal is also to tie a manufacturer of equipment to the project. The target is to recover the maximum amount (near 100%) of tungsten from the Scheelite concentrate.
7. References

[16] Ultrasonic disintegration — ULTRAWAVES. http://www.ultrawaves.de/technology/ultrasonic-disintegration