GEOTHERMAL BRINES – HIGH VALUE MINERAL EXTRACTION

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In-situ reactions, Geothermal brines, Precipitation, High value precipitates

Abstract

Hydrothermal brines are extracted from significant depths below the surface of the earth and arrive at the surface at elevated pressure and temperature. The exact chemistry and conditions of these brines depends upon the rock formations through which the water travels, but many of the brines are rich in dissolved minerals especially silica which is often saturated in the brine. At pressure and temperature the minerals remain in solution but in order to extract heat from the brines, they need to be cooled and during which many of the minerals precipitate causing problems. Where precipitation is a problem in the downstream processing, the brines are maintained at a high enough temperature and pressure so as to avoid precipitation and injected back into the geothermal formation. This results in a significant loss in potential energy that could be recovered from the geothermal brines.

If left to precipitate in an uncontrolled manner, many of the minerals will precipitate as gels, in a high surface area form which is difficult to extract from the liquor and which can causes problems. Precipitation in this manner often builds up on the inside of pipes, reducing the pipe cross-section available for fluid flow and reducing the overall efficiency of the plant. If the brines are seeded at the appropriate time or the precipitation conditions are changed, mineral particles can be grown and separated more easily from the brine. During this precipitation and growth phase the chemistry of the local environment can also be altered to grow more valuable particulates. Some of the specific chemistries will be discussed with reference to known geothermal brines and what needs to be done to precipitate value added products. A theoretical approach to the complete extraction of minerals from geothermal brines is also discussed with the goal of extracting more heat from the brine prior to reinjection into the well.

Introduction

The earth’s core is significantly hotter than the surface which continuously radiates heat into space. Consequently for every 100m we go down into the earth from the surface there is an average increase in temperature of approximately 2.5°C to 3°C. Given a nominal surface temperature it is estimated that the temperature increases to an average of approximately 70°C at 2000m and about 100°C at 3000m depth. While this is depicted as the average value there are many places on the earth where the gradient is significantly less than the average where new sediments have been laid down reducing the gradient to less than 1°C per 100m. Likewise in volcanically active regions this gradient can be significantly increased to over 10°C per 100m.

Geothermal Brines

Around the world many of these geothermally active sites are being used to generate thermal energy for a wide range of applications. Typically a fluid is used to extract the heat from the ground – bringing it to the surface where it can be converted into a more useable form of energy. These geothermal fluids are usually naturally occurring water and if they are removed (for heat extraction) must be reinjected into the ground to maintain equilibrium. The hot water in contact with indigenous rocks readily leaches minerals from the rock causing it to form a brine rich in soluble mineral salts. Silica is the most readily leached mineral and most brines quickly becomes saturated in silica.

During heat recovery, the geothermal brines are cooled causing them to supersaturate and precipitate silica This poses a serious problem for many operations which transport several thousands of liters of brines per minute through them, and can cause blockages due to build up of silica based deposits on the pipes. One approach for the use of geothermal energy to drive turbines and generate electricity has been to limit the temperature drop such that the precipitation of silica is minimal (and therefore manageable), but this has a significant impact on the efficiency of the geothermal well since the saturated brine (still containing significant thermal energy) is injected back into the ground.

More recently these geothermal brines have been considered as mineral resources since many of the chemical constituents in geothermal fluids are a potential source of valuable minerals and metals. Recovery of minerals and metals from geothermal fluids can be viewed as "solution mining by nature" followed by application of established or new hydro-metallurgical techniques for isolation and purification [1]. The first application of such "mining" techniques took place at Larderello, Italy, as early as the turn of the last century where boric acid was extracted from geothermal steam [2]. Some geothermal fields such as those found in the Salton Sea, Brawly and Niland in the U. S., the Milos field in Greece, the Assal field in Djibouti and the Cheleken geothermal field in Russia, to mention only a few, contain significantly rich mineral brines to make them potentially economically viable sources of some minerals. For example, a 50 MWe geothermal power plant could have as much as 35,000 m^3 of brine pass through the facility daily. At a concentration of only 1 mg/kg approximately 30 kg of metal passes through the facility each day [3] making the amount of recoverable minerals large despite relatively low concentrations.

Minerals of primary interest include silica, zinc, lithium, manganese and a number of rare earths. Some brines may even contain significantly high concentrations of precious metals such as silver, gold, palladium and platinum to make recovery potentially attractive.

Commercial Production of Precipitated Silica

There are several operations within the US that have developed a process for the extraction of silica from geothermal brines. In solution the silica is present as a monomer which, as concentration increases, reacts to form polymers as shown in Figure 1. With increasing concentrations further polymerization forms large chains of silica based hydrates which eventually form colloids. These colloids have the ability to nucleate out as precipitates onto any surface which is presented to them thereby forming scale on the inside of pipes, restricting flow and eventually rendering the process inoperable. Selected geothermal operations have intentionally investigated the precipitation and removal of silica from the geothermal brine in an attempt to reduce scaling. The revenue stream [4] based on a 50 MWe power plant in the Salton Sea geothermal field could provide as much as 10.2 million dollars per year while a similarly sized facility at the Coso, CA, geothermal field could result in a revenue stream of up to 12.9 million dollars per year. These figures are based on a 60% silica recovery rate and a selling price of $2,200 per metric ton and a plant capacity factor of 95%. More recently, the inherent mineral value (in additional to silica) within the brine have also been considered [5].

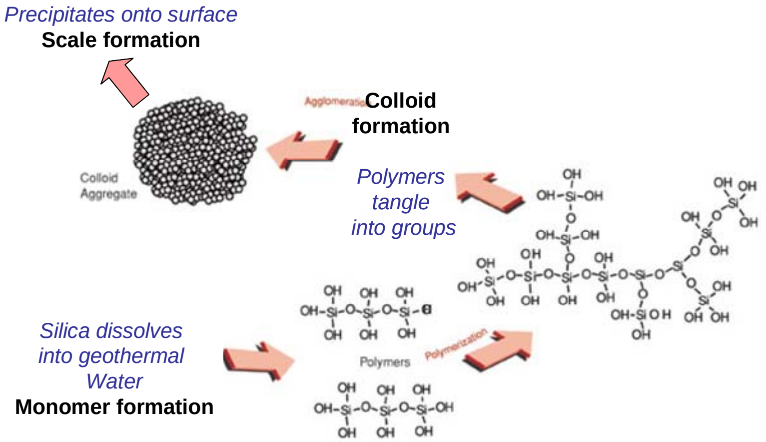

Figure 1. Illustration showing the sequential formation of silica scale from brines.

The U.S. Department of Energy's Brookhaven National Laboratory, in collaboration with Caithness Operating Company of Reno, Nevada, won a 2001 R&D 100 Award for developing a technology to recover commercial-quality silica from geothermal brine, a byproduct of geothermal energy production [6]. Retrieving this valuable product from brine, which is generally disposed of as waste, results in cheaper energy production [7].

Silica is used widely as a drying agent for products such as salt; a polishing agent for commodities such as toothpaste; as a filler, extender or reinforcer for plastics, paper, paint and rubber; and as a catalyst for refining oil. It also has applications in fiber optics and in nanoscience. Previous research at Brookhaven focused on silica recovered from high-salinity goethermal brines that contain many impurities. These impurities may include iron, as well as other metal salts such as zinc and manganese, and have to be removed at high cost in order to produce marketable silica. In contrast, the new Brookhaven/Caithness technology recovers silica from low-salinity brines that contain very few impurities. Since the recovered silica using the new process is 99.9 percent pure - much purer than most silica on the market today - new uses may be found for it, including chemical production. The process flow diagram for the silica precipitation process is shown in Figure 2.

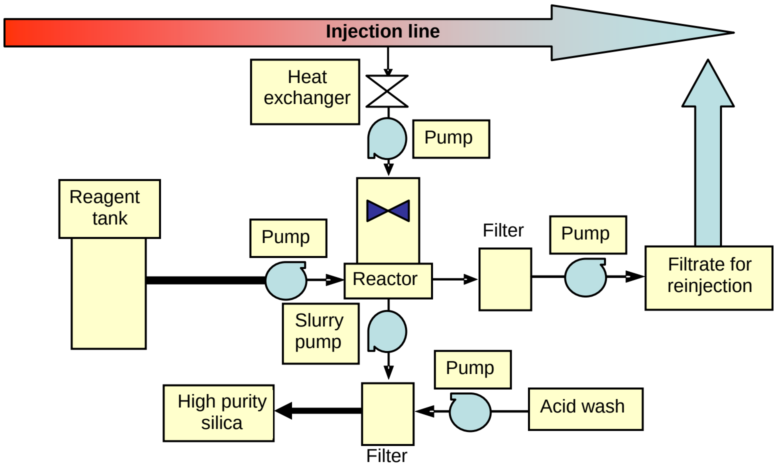

Figure 2. Flow diagram for the precipitation of high purity silica from geothermal brines.

In the new Brookhaven/Caithness silica recovery technology [6] the brine is first brought into a “controlled” condition by filtering it at a high temperature to remove all particulates present. The pH is controlled and the silica precipitated under controlled conditions. The production of very pure and relatively inexpensive silica may lead to refinement of existing products, particularly in nanoscale materials, like chips for sub-micron electronic circuits. The conventional process for producing silica involves fusion of silica sand with alkali to make silicate. The alkali silicate is then neutralized with acid yielding precipitated silica. The product is costly when compared with the Brookhaven/Caithness process, which is based on precipitation. A chemical reactor especially developed for the process precipitates the silica from geothermal brine under specific processing conditions. Table I shows the surface area, pore size and volume for silicas precipitated from a range of US geothermal brines.

Table I. Physical properties of silica precipitated from a range of geothermal brines

Property	Commercial	Beowave	Coso	Dixie Valley	Steamboat
BET surface area (m^2/g)	237	517	269	490	52
Total pore volume (ml/g)	1.3	0.4	0.53	1.0	0.62
Pore diameter (nm)	>100	6	14	30	9.2

Past Experience with In-Situ Hydrothermal Reactions

There are a number of reactions which have been performed on brines at elevated temperatures and pressures which might be directly transferable to the geothermal brine systems. However, much of the specific processing which can be done will depend upon the conditions of the brine, the available mineral concentrations and on the desired product.

Chemical reduction and crystal growth in Bayer Liquors.

Although direct conversion of silica based brines has not yet been reported, previous experience in the in-situ reaction of hydrothermal systems has been investigated with the digestion of bauxite (mixed aluminum, iron hydrated oxide) and precipitating red-muds from Bayer liquors. In the Bayer liquor, geothite (FeOOH)) was insoluble but needed to be efficiently removed from the liquor to enable the controlled precipitation of the alumina salts. Under normal alkaline conditions the geothite was very microcrystalline (and possibly amorphous) in nature giving rise to a specific surface area (SSA) of several hundred m^2/g. This in turn was very difficult to remove from the liquor due to very slow settling rates. In this work high surface area geothite and hematite particles, with poor crystal structure, were reduced to magnetite particles with very good crystal structure as shown in Figures 3 and 4. This reduction was brought about by the addition of sugars, organic oils, Al or Mg metals and reduced the specific surface areas from around $100m^2/g$ to less than $10m^2/g$ under the same conditions of temperature, pressure and time. Higher temperatures and higher concentrations of reducing agents have allowed significant reduction and growth of magnetite crystals as shown in Figure 5. The magnetite produced at 250°C with 10g/L sugars could be readily sedimented through their high specific gravity or could be extracted from the liquor my magnetic separation [8].

Figure 3. At 200°C, >10 g/L sugar for 2 hrs – magnetite and hematite formed from geothite. Under these conditions, magnetite can be fully substituted with Zn ($ZnFe_2O_4$) and hematite can be substituted with Al. (390°F, ~300 psi)

Figure 4. At 250°C, magnetite formation is far more extensive. At 10 g/L either Al or sugar, magnetite ($ZnFe_2O_4$) and hematite are formed. If lime is not added – hematite formation is negligible. (480°F, ~400 psi)

For the reduction of many metal based oxides, sufficient thermal energy is available within the leach liquor. This is also the case for many geothermal brines where reduction of crystal growth might be desired. Other reactions, such as the formation of carbides or nitrides from the silica rich brines would probably require addition energy to drive the reaction. This could be achieved through the addition of ultrasonic energy.

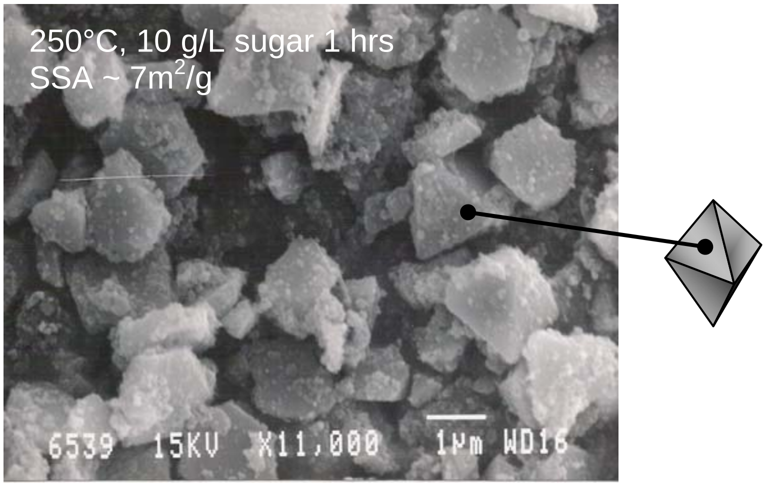

Figure 5. Electron micrographs of reduced iron hydroxides and oxides with Al or sugar additives. Note the blocky formation of large characteristic magnetite particles formed at high temperature with a larger amount of reducing agent.

<u>Hydrothermal growth of anhydrous carbonates</u>.

Nesquehonite ($MgCO_3.3H_2O$) shown in Figure 6 is a naturally occurring mineral which can be used as a source of magnesium. Unfortunately the raw material contains significant amounts of water which are difficult to remove and inhibit the use of this mineral from being used directly for magnesium production, due to the introiduction of significant oxygen. Processing of the mineral under atmospheric conditions or brief hydrothermal conditions 180°C, 1.6 MPa for 15 minutes and quenched (356°F, 240 psi) results in the formation of hydromagnesite

($5MgO.4CO_2.5H_2O$) shown in Figure 7 which still contains significant water and cannot be calcined directly to MgO. If however, the nesquihonite is processed for 8 hours under these conditions anhydrous magnesium carbonate is formed as shown in Figure 8. This anhydrous magnesium carbonate is calcined at 600°C it forms nano-crystalline MgO shown in Figure 9 which can be used directly for the production of magnesium metal through the chloride route.

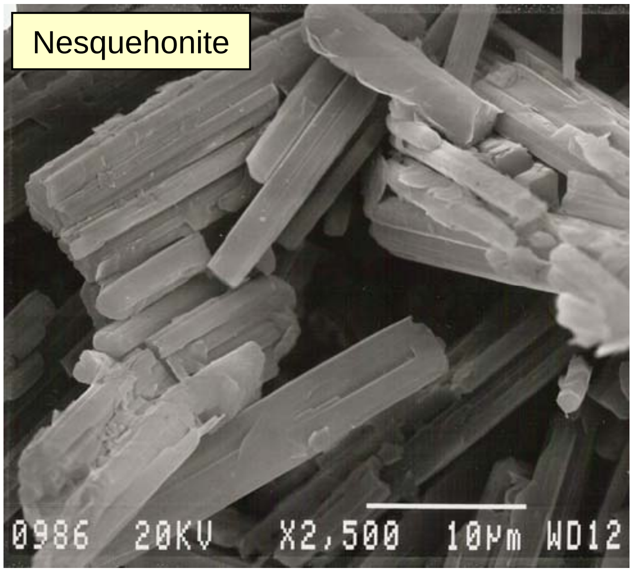

Figure 6. Natural nesquihonite – rich in magnesium but difficult to process

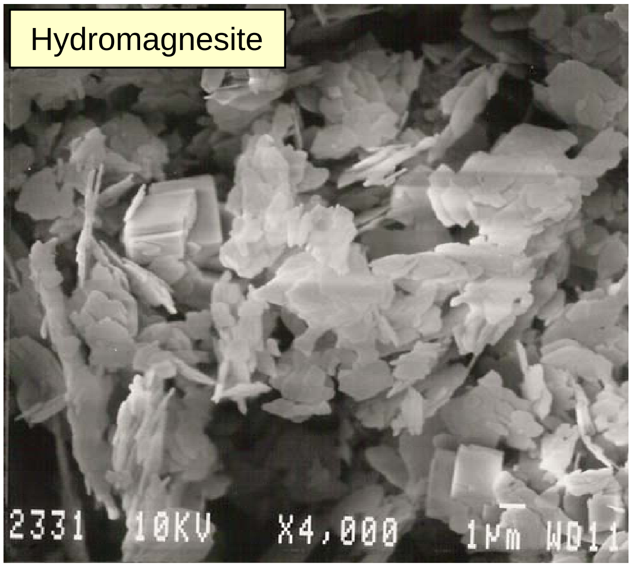

Figure 7. Plate-like hydromagnesite – still contains significant water

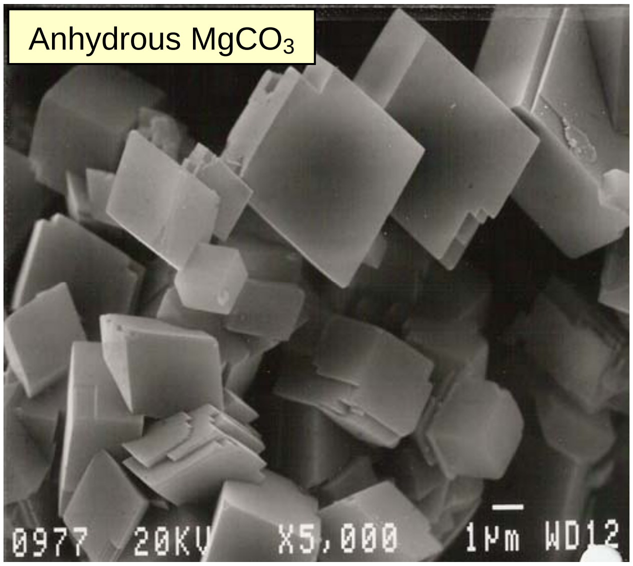

Figure 8. Under hydrothermal conditions and with extended processing times anhydrous $MgCO_3$ can be formed

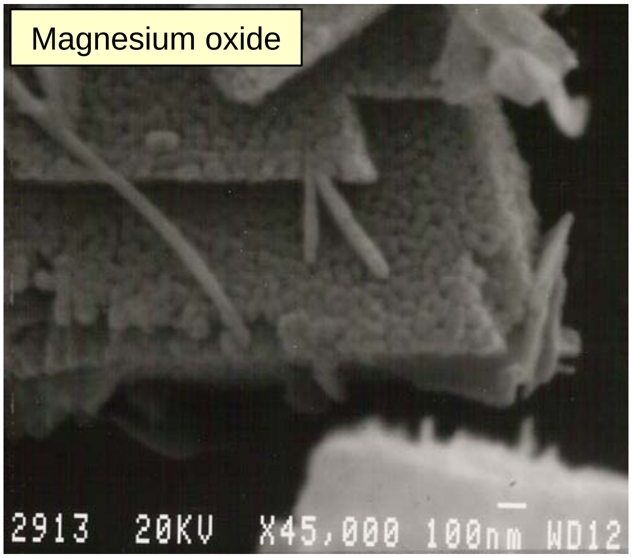

Figure 9. The anhydrous $MgCO_3$ can be directly calcined to a MgO feedstock

This work maybe important since it illustrates how the CO_2 overpressure, although unexpected, allows the formation of anhydrous carbonates while being hydrothermally processed. Similarly with geothermal brines it maybe possible to inject CO_2 under pressure to ensure the formation of desired, high value, anhydrous carbonate products [8].

Potential In-Situ Reactions for Geothermal Brines

There are really two concerns which need to be addressed in the mineral extraction from hydrothermal brines. The first is the chemical reaction, precipitation and crystal growth of the desired product phases. The second is the efficient removal of the particles from the brine stream. Regarding the first of these concerns there is a significant amount of energy (both thermal and pressure) present within the geothermal brines which can drive many of the desired reactions, and if additional energy is required it can be introduced effectively in many ways. Ultrasonic energy addition however, is one approach being addressed since it allows the deposition of large amounts of energy and can be well controlled even within the context of a hostile processing environment.

Building on existing silica precipitation knowledge from Brookhaven National Laboratory, and Lawrence Livermore National Laboratory it is proposed that by changing the brine chemistry and energy state, the high purity silica can be further reacted in-situ to form higher value products such as SiOC, SiC, Si_3N_4, SiAlON, SiB_6 or SiB_4 [8]. Although the thermal energy available (even in very high temperature/high pressure brines), is insufficient for many of the desired reactions such as;

$$SiO_2 + CH_4 \Rightarrow SiC + 2H_2O$$
$$3SiO_2 + 4NH_4OH \Rightarrow Si_3N_4 + 10H_2O$$

Additional energy can be efficiently supplied through ultrasonic energy, to ensure that the desired reactions are favored. This will allow the geothermal brines to be converted directly to high value added nano-particles. The chemical constituents will be added directly as secondary reagents in the brine (either by bubbling gas, or adding nitrates, nitrides in the form of ammonium compounds, or boranes) so that nitrides, carbides and diborides can be produced directly.

Two approaches could be investigated; the first through a gaseous introduction of carbon (as methane for instance) and the second through the addition of a liquid carbon source such as sugar. Both of these approaches are illustrated in Figure 10 below where the individual silica sols which form are surrounded by the carbon containing species. The ultrasonic levels could be monitored to determine the threshold level beyond which the silica reacts to form an amorphous SiC phase. Similar experiments could be performed to generate silicon nitride in the presence of ammonia.

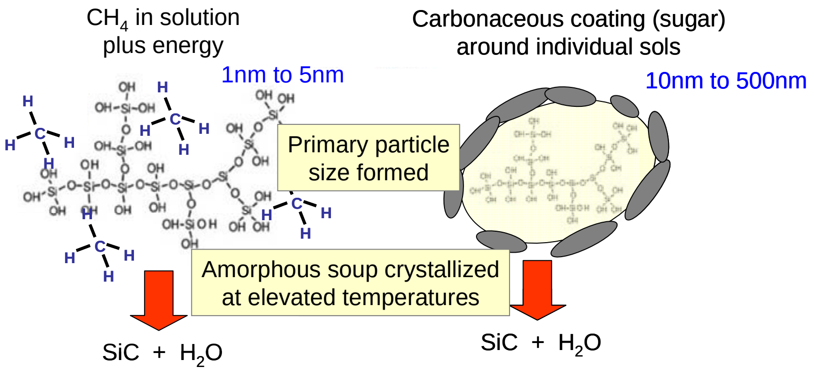

Figure 10. Illustration showing the formation of the individual silica sols and the surrounding by carbon containing phases – either as a gas (left) or as a liquid (right). The gas approach should form smaller individual particles.

In addition, the local chemistry can be changed by the addition of other finely dispersed or soluble minerals which have demonstrated the ability to act as sponges for other trace minerals such as the Zn, Fe spinel shown in Figure 3. For the efficient extraction of minerals from the brine liquor a significant degree of understanding is required about the interaction, concentrations and solubilities of the various mineral constituents so that a designed and sequential extraction series can be achieved.

Additional mineral phases may also be added to achieve selected seeding and separation from the brines. For instance, given the high temperature and pressure within many of the geothermal brines the addition of low cost geothite may allow the formation of small seeds of magnetite under the correct reducing conditions, which with a reduction in temperature could be used as seeds for the precipitation of a second phase. These particles could readily be removed from the brine stream using magnetic separation techniques. Similarly, small particles of a high specific density material such as WC could be used as seeds for growth of a second phase and effectively separated from the liquor using hydrocyclones.

Expected Outcome

It is expected that with moderate ultrasonic power, under reactive conditions the silica brine should be readily transformed into silicon carbide (carbon based additives) or silicon nitride (nitrogen (ammonia) based additives), and that these particles will be high purity and nano-scale suitable for sale to the ceramics industry. With in-depth knowledge of the geothermal brine constituents and their relative solubility, it should be possible to design a comprehensive extraction methodology that can remove important mineral from the brine as well as allow an increase in the heat extraction from the geothermal brine to be achieved. In the future a sequential transformation of selected minerals might be possible for a given geothermal brine feedstock as illustrated in the cartoon shown in Figure 11. Depending on the brine composition it maybe possible to sequentially extract a series of minerals using magnetic seed materials for instance which could be completely extracted from the liquor stream once they had been coated.

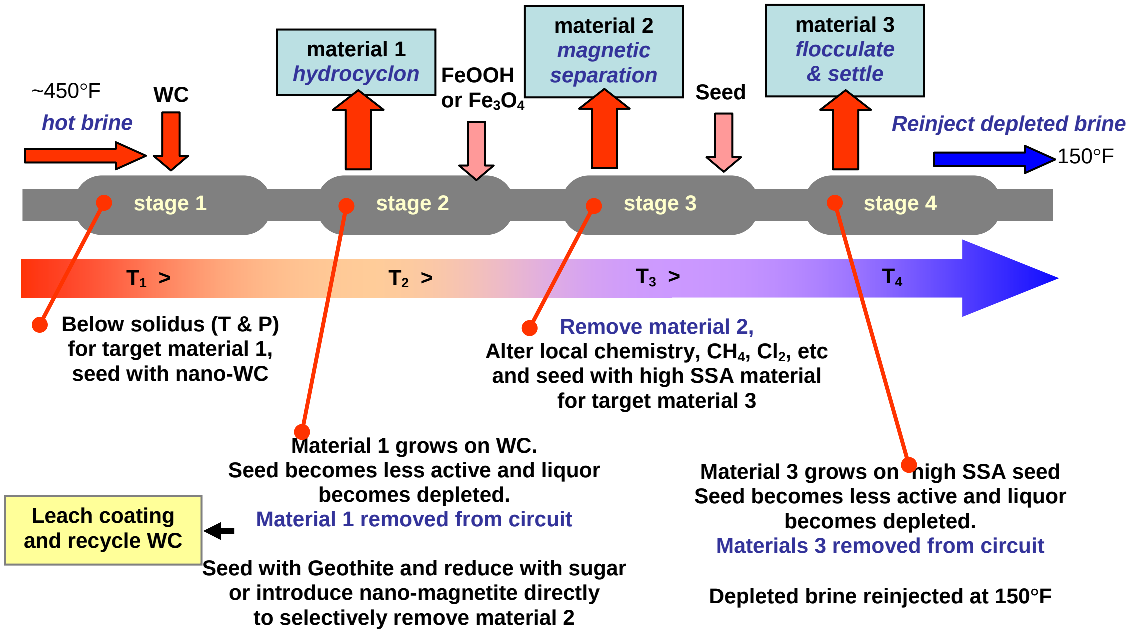

Figure 11. Future processing approach for the sequential separation and transformation of minerals from a given geothermal brine.

Discussion and Conclusions

The approaches described above draw from past knowledge with hydrothermal systems. One example shows how a CO_2 overpressure allows us to alter the stable carbon containing phases formed while the other example shows how small additions to Bayer liquor brines can completely change the precipitate morphology and chemical composition, thereby increasing their value and making their separation from the liquor far easier. It is proposed that these and other approaches can be used with geothermal brines to aid in the mineral recovery and separation.

An assessment of the present energy usage in the mining, grinding, liberation and concentration of minerals in Figure 12 shows how the energy usage is distributed among the different tasks. In comparison it is estimated that mineral concentrates formed directly from geothermal brines would represent an energy savings of at least 70% since the highly energy intensive crushing, grinding and digestion stages are not required. Additionally, using the energy inherent in the geothermal brines (or through the addition of a small amount of additional energy) it maybe possible to transform otherwise low value products such as SiO_2 to significantly higher value precipitates such as SiC and Si_3N_4.

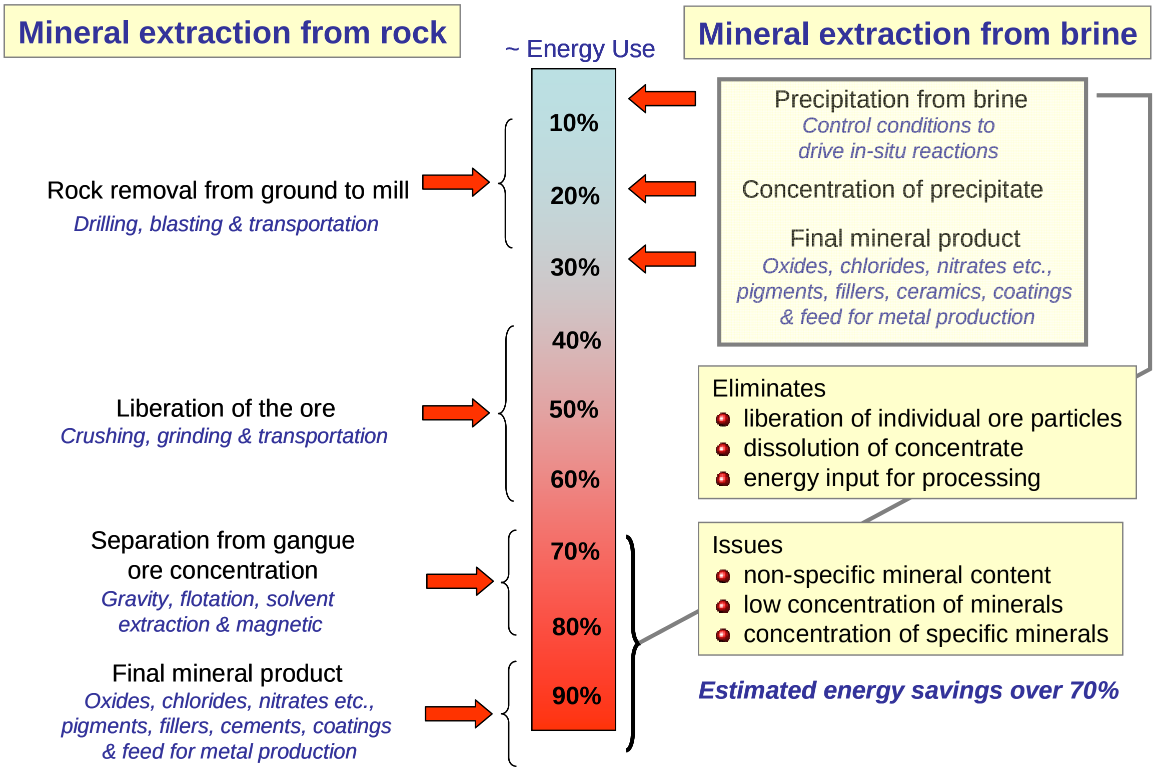

Figure 12. Illustration comparing the energy use in conventional mineral extraction from rock with that of mineral extraction from geothermal brines. This fairly simple analysis estimates at least a 70% savings in energy consumption.

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