Geothermal Brines: A New Source of Commercially Valuable High Grade Silica

Eugene T. Premuzic, Brookhaven National Laboratory, Upton, New York 11973

Abstract

An in depth, multi year R&D program dealing with geothermal residues and wastes has led to the development of processes and technologies for the conversion of precipitated wastes and brines, generated by geothermal power plants to useful and commercially attractive by products. Thus, high salinity brines and residues with significant concentrations of metal salts, silicates and in some cases, radioactive materials, were converted to environmentally acceptable wastes available to further processing and production of useful materials. Similarly, silica extraction from low salinity brines reduces the scaling problems and further treatment yields high grade silica, with many applications in the production of fine chemicals and other commercially valuable products. In this paper some of the above topics will be discussed.

Hot water and steam resources are found in many subsurface locations of the world (Geothermal Energy 1996, Freeston, 1996). Depending on the chemistry, the steam/water system emerging from surface production wells can be used directly or separately as an energy source for the production of electric power. Compared to coal, oil and gas resources, geothermal energy is a clean source of electric power and does not produce emissions of sulfur and nitrogen oxides. However, on cooling the brines generate residues as well as scaling of equipment. Further, there are significant chemical differences between high salinity and low salinity brines and variations in chemical composition from one geographical location to another (Premuzic et al., 1989). Thus, high salinity brines produce a sludge which contains a mixture of toxic and valuable metals. Such residues require detoxification because they are considered mixed wastes and, therefore, subject to regulatory requirements (Royce, 1985). Our first task was to search for cost-efficient and environmentally acceptable technology which would enable the removal of toxic metals from geothermal brines and sludges. Extensive studies at Brookhaven National Laboratory (Premuzic et al., 1987, 1988, 1995, and references therein) have shown that a biochemical technology for the treatment of brines and sludges derived from high salinity geothermal sources is most promising, cost-efficient, and environmentally acceptable. The technology depends on the chemistry of the resources which influence the choice of plant design and operating strategies. Further, a number of process variables had to be taken into consideration in the design and engineering of the total process as well as in the cost-analysis. The parameters which had to be considered included rates of input, volume, batch, or continuous processing, residence times, recycling of biocatalysts, corrosion and the chemical characteristics of the incoming materials and those of the end products. Further, the technology had to be flexible and adaptable to variables such as high and low salinities. A typical process design is shown in Figure 1 (see also Premuzic et al., 1995). This is an example for a process designed for the treatment of quantities of about one tone per hour of filtered sludge. In the course of R&D of this technology other options have also become apparent. These include metals and salt recovery as well as strategies which would lead to utilization of the residues from which toxic and valuable metals have been removed, silica being of particulate interest. In the example shown in Figure 1, streams A and B are combined for metal recovery, where stream A is derived from the plant and stream B is derived from the biochemical reactor via stream 9 in which the solids are removed and the filtrate stored in tank B. It is to be noted that in the earlier version, the filtrate which contains metals was neutralized with calcium hydroxide, the precipitate filtered and the aqueous phase reinjected. There were obvious disadvantages to this approach. Precipitate in stream 14, although greatly reduced in volume correspond to that generated in stream 10, had to be disposed of. Maintaining an appropriate anionic and cationic concentration allows to pool stream 11 from the holding tank B with stream A with the full elimination of all the steps beyond B. In the removal of metals in general and particularly toxic ones from high salinity brines, in some cases attention had to be paid to the presence of certain radionuclides. A secondary biochemical treatment of the brine/sludge after the treatment described above was developed and the results are summarized for the "untreated" and "treated" residues in Table 1. The chemical and physical properties of the processed material can be manipulated to generate commercially attractive products such as paint fillers, quality silica and others. Historically speaking, at this stage of R&D which dealt with the treatment of geothermal brines we were ready to address Task 2, namely, the recovery of silica. Silica occurs as a dissolved species in all liquid dominated geothermal resources (Premuzic et al., 1999). The circulating hot geothermal fluids dissolve silica from rock formation, and generally achieve saturation relative to quartz and other mineral species in high temperature systems. The concentration of silica varies, and higher concentration would be attractive in terms of silica recovery per volume of brine processed. However, concentration alone does not determine the quality of silica nor the economic attractiveness of a silica recovery process. The salinity range found in geothermal systems varies from several hundred to several thousand parts per million. High salinity systems promote diverse ion interactions and incorporation of a wide range of ionic species into silica precipitates, while the relatively simpler chemistry of low salinity systems allows for the isolation of high purity silica with fewer processing steps. Co-production of such silica would lower the cost of power production, because high quality silica can generate a significant secondary income and also the removal of silica minimizes scale formation and consequently allows for more cost-efficient energy production capabilities (Premuzic et al., 1999, Lin et al., 2002). Silica has many applications such as in fillers for paints, rubber, powders and others. Compared to high salinity brines silica production from low salinity brines has an advantage, because it requires fewer processing steps that lead to high quality chromatographic grade silica. Composition of commercial and high grade geothermal silica (GTS) is given in Table 2. GTS silica can compete directly with commercial silica used for thin layer chromatography and process chromatography with annual sales of about $240 million. Table 3 shows potential silica recovery from low salinity brines, which means for example, the product from Dixie Valley would compare to a product (15 micron pore diameter) with a current retail value of $1000 for 25 Kg lots, and as Table 4 indicates, the market prospects are very promising. A concerted effort is now being pursued to make the potential GTS production a market reality.

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Table 1. Biochemical Removal of Radium and Thorium from Geothermal Sludges Subjected to Secondary Treatment

	RA-223	Ra-224	Ra-226 µCi/g	Th-232	Total Activity
Untreated (Total Sample)	2.63×10^{-5}	6.46×10^{-4}	2.8×10^{-4}	1.8×10^{-4}	2.82×10^{-3}
			Treated with BNL MOs		
BNL-R_x-1	4.35×10^{-5}	6.46×10^{-4}	2.8×10^{-4}	1.8×10^{-4}	2.89×10^{-3}
BNL-R_x-2	3.3×10^{-5}	n.d.	n.d.	n.d.	1.31×10^{-3}
BNL-R_x-3	n.d.	n.d.	n.d.	n.d.	1.31×10^{-3}
BNL-R_x-4	n.d.	n.d.	n.d.	n.d.	1.27×10^{-3}

Table 2. Quality Comparison of Precipitated GTS Silica with the Commercial Product

	Commercial Silica	GTS Silica
BET Surface Area (m2/g)	240	520
Total Pore Volume (ml/g)	1.3	0.41
Pore Diameter (nm)	100	7.68
Agglomerate Size (micons)	50-100	5-15

Table 3. GTS Silica Recovery

Brine Concentration	600-pppm
% Recovery	66%
For 50 MW Power Plant	6000 t/y

Table 4. Market for Precipitated and Colloidal Silica

Precipitated Silica	190,000 tons
Colloidal Silica	68,000 tons
Annual Market Growth	4%
Value Range in $	$1/lb to $100/lb