Reducing Foreign Lithium Dependence through Co-Production of Lithium from Geothermal Brine

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ABSTRACT

Following a 2009 investment of $32.9 billion in renewable energy and energy efficiency research through the American Recovery and Reinvestment Act, President Obama in his January 2011 State of the Union address promised deployment of one million electric vehicles by 2015 and 80% clean energy by 2035. The United States seems poised to usher in its bright energy future, but in reality, industry supply chains still rely on foreign sources for many key feedstock materials. In particular, 43% of the lithium consumed domestically is imported, primarily from Chile, Argentina and China, and in 2010, only one company produced lithium from U.S. resources (USGS, 2011).

Geothermal brines of the Imperial Valley resources of Southern California have been shown to be especially enriched in lithium but today remain an untapped resource. Producing lithium battery feedstocks at geothermal production facilities could not only provide the U.S. with much-needed lithium products and by-products, but could provide millions of dollars in added revenue to geothermal developers.

By providing lithium reserve estimates, Imperial Valley production potential and forecasts of the future of the electric vehicles industry, this study aims to relate the imperative of domestic lithium production to the vast potential of U.S. geothermal resources and showcase the benefits of industry adoption of lithium co-production at viable geothermal power plants.

1. Introduction

The vast potential for mineral recovery from geothermal fluids has been recognized for decades. Beginning in the 1970s with potash extraction from Cerro Prieto, Mexico, metal and mineral extraction techniques have been demonstrated at a wide array of resources and today represent a promising means of producing metals and materials imperative to the rapidly developing clean energy industries in the United States.

Today, 43% of the lithium consumed domestically is imported, primarily from Chile, Argentina and China, and in 2010, only one company produced lithium from U.S. resources (USGS, 2011). From 1996 to 2005, apparent lithium consumption in the U.S. more than tripled (Wilburn, 2008) and is projected to increase dramatically with increased manufacture and demand for lithium ion batteries for use in electric-drive vehicles. Actual imports and consumption are higher because we also import lithium-containing batteries and devices containing batteries for use.

With 4,000,000 tons of estimated resources, 38,000 of which are currently economically attractive (see Table 2), there is no reason for the U.S. to be as reliant on foreign lithium sources as it is today. Decades of research and an ongoing lithium extraction pilot in Southern California show promise for this industry, and if proven to be technically feasible and financially competitive on a commercial scale, the adoption of co-production of lithium at geothermal plants has the potential to significantly reduce our dependence on foreign lithium sources.

2. Overview of Metal Extraction

Geothermal fluid, or “geofluid,” is the hot brine pumped from depth to the surface at geothermal production facilities. In a typical production scenario, after energy is extracted, the now-cooled “spent brine” is reinjected into the reservoir in a continuous loop. Mineral extraction methods are applied to spent brine, downstream from power production and just prior to reinjection into the reservoir. The symbiosis of material extraction facilities at operating geothermal power plants is ideal because the infrastructure for fluid flow-through and processing is largely already in place, and the royalties from the sale of by-products can provide an added revenue stream for the developers.

While the lithium dominating the market today was produced by brine evaporation and hard-rock mining methods, recovery from geothermal fluids involves a variety of chemical extraction techniques which operate quickly and without losing substantial fluid volume. Lithium can be extracted from geofluids using ion exchange resins or through the use of sorbents and stripping solutions (Bourcier et al., 2005).

Some of the earliest attempts at mineral extraction targeted silica, SiO_2, with the goal of producing high-purity colloidal silica and other commercial silica products. Other materials that have been attempted include zinc and potash. A variety of pilot extraction plants have come online in the past few decades in Nevada and California, many of which were supported by partnerships with the Department of Energy, Lawrence Livermore and Brookhaven National Laboratories, but none have enjoyed commercial success.

The closest that mineral recovery has come to commercial sustainability in the U.S. was a zinc extraction operation that came online at a CalEnergy facility in the Imperial Valley, CA. As a demonstration plant in the late 90s, this operation produced over 41,000 lbs of high-grade metallic zinc over the course of 10 months (Kagel, 2008). In the early 2000s, this demonstration scaled up to a commercial plant expected to annually produce 30,000 metric tons of 99.99% pure zinc (Clutter, 2000), but the project experienced operational and financial difficulties and was shut down within two years in 2004 (Kagel, 2008).

Today, another attempt at metal extraction is underway in the Imperial Valley. Start-up company Simbol Materials has a site access agreement with CalEnergy to operate a pilot lithium extraction plant at Elmore, where zinc extraction was attempted in 2002. If the pilot is successful, Simbol hopes to begin extracting lithium at a commercial scale in the Imperial Valley, validating these methods as a potentially significant supply of strategic metals.

3. Geochemistry of Geothermal Brines

Due to variations in depth, fluid source, host rock and rock-fluid interactions in different geological regimes, geofluids exhibit a wide distribution of properties. Acidities range from pH 5 to 9 (Bourcier et al, 2005), while economically viable temperatures range from ~200ºF (~93°C) and higher (Kagel, 2008). Total dissolved solids (TDS) typically range from 1,000 to 300,000 parts per million (ppm) (Bourcier et al, 2005), but have been shown to vary according to well flow rate and from location to location within a resource (Maimoni, 1982). Brine chemistries are also known to differ in pre-flash and post-flash fluids from the same well (Maimoni, 1982).

The most common elements in geothermal brines are consistently sodium, calcium, potassium and chlorine, in concentrations ranging from tens to tens of thousands of ppm . Present in significant but lesser amounts are other alkali metals, alkaline earth metals, and halides. Lithium concentrations can vary by orders of magnitude and will be discussed in more detail in the next section. Ore and base metals such as iron, manganese, zinc, lead and copper are variably present, while precious metals such as silver, gold, platinum and palladium are typically present only in concentrations of parts per billion and commonly escape detection entirely. The highest concentrations of base and precious metals tend to be in hyper-saline brines. Silica is ubiquitous in geofluids, typically in the range of 400-800 ppm (Gallup, 1998). Table 1 shows representative elemental concentrations from a selection of geothermal resources.

4. The Potential for Lithium Recovery in the Imperial Valley[1]

Some of the most mineral-rich and highly studied geothermal reservoirs in the United States are located in the Imperial Valley of Southern California. With TDS ranging from 200,000-250,000 ppm in the deeper brine reservoir (Schultze & Bauer, 1982), Salton Sea brines in particular contain a veritable treasure trove of valuable metals and minerals.

The prospect of estimating a total lithium resource in the Imperial Valley is contentious. It is easier, instead, to evaluate the potential for lithium production at a representative Salton Sea power plant producing 40MW of electricity. For the purposes of this paper, a conservative estimate of lithium reserves will be proposed, with the caveat that there is tremendous potential for higher returns.

As can be seen in Table 1, lithium in the Imperial Valley resource areas is present in much greater amounts to orders of magnitudes above those in other resources. In the Salton Sea in particular, Schultze & Bauer (1982) in published a "typical" lithium concentration of 170ppm, and Maimoni (1982) attained a broad range of 117-245ppm from two wells. In this calculation, the outliers presented here will be disregarded and average lithium concentration will be considered to be 170ppm.

Due to the commonly proprietary nature of flow tests, some discrepancies exist regarding the flow rate needed to maintain

Table 1. Results from Geochemical Analyses of Geothermal Fluids (Gallup, 1998).

Species (ppm)	Salton Sea, CA	Brawley, CA	Imperial Valley, CA	Coso, CA	Dixie Valley, NV	Roosevelt, UT	Mississippi Salt Dome Basin, USA	Wairakei, New Zealand	Asal, Djibouti	Milos, Greece	Cheleken Peninsula, Turkmenistan
Li	194	219	327	45	2	27	N/A	13	N/A	81	215
Na	53,000	47,600	65,500	2,850	407	2,190	59,200	1,250	29,000	31,500	76,140
K	16,700	12,600	12,450	927	64	400	538	210	5,500	9,500	409
Rb	170	67	N/A	N/A	N/A	N/A	N/A	3	N/A	N/A	N/A
Cs	20	19	N/A	N/A	N/A	N/A	N/A	3	N/A	N/A	14
Mg	33	114	400	<0.35	0	0	1,730	N/A	30	4	54
Ca	27,400	21,500	23,700	75	8	10	36,400	12	18,500	4,380	19,710
Sr	411	1,043	N/A	3	0	1	1,100	N/A	N/A	70	400
Ba	203	992	2,260	N/A	N/A	N/A	61	N/A	N/A	37	235
Fe	1,560	3,733	4,160	N/A	<0.01	N/A	298	<0.01	N/A	19	2,290
Al	2	1	4	N/A	2	N/A	N/A	N/A	N/A	N/A	N/A
Cl	151,000	134,000	131,000	5,730	438	3,650	158,200	2,210	81,000	65,400	157,000

40MW of electrical production. In a 2010 press release, Ram Power announced that its Orita #2 well in the Imperial Valley had sustained a steam flow rate of 500,000 lbs/hr and was estimated to provide 8-10 MW of power. Scaling this up linearly, one could expect a flow rate of approximately 2 million lbs/hr of fluid at a typical 40MW geothermal plant. A 2009 report by the California Division of Oil, Gas and Geothermal Resources reports average flow rates of 3-4 million lbs/hr, for a typical 40MW plant. As a highly conservative estimate, the former figure of 2 million lbs/hr will be used.

The process for extracting lithium from the brine has yet to be validated on a large-scale, long-term basis. While an ideal case would yield >90% lithium recovery, in this scenario it will be estimated at 75%. The conversion factor from lithium metal to lithium carbonate is stoichiometrically rounded to 5.32

With all of these assumptions in place, a typical 40MW plant in the Imperial Valley resource areas could expect to produce at least 5,400 metric tons of lithium carbonate annually from extracted lithium chloride. If the value of lithium carbonate remains at its current market price of ~$5,000/metric ton (Ehren, 2009) the minimum gross annual revenue from a single 40MW plant would start at ~$28 million. Because published data indicate the likelihood of higher flow rates and higher lithium concentrations in the brine, actual produced lithium and revenues could prove to be much higher than expected. Wild cards in this scenario are the lithium recovery rate and purity of produced lithium carbonate, which have yet to be validated.

5. The Current State of Lithium Production

Lithium and lithium compounds are utilized in a wide variety of industrial products. Industry-ready lithium materials include lithium compounds and lithium ore concentrates. In 2009, global end-use markets for lithium were as follows: 31% for ceramics and glass, 23% for batteries, 9% for lubricating greases, 6% for air treatment, 6% for primary aluminum production, 4% for continuous casting, 4% for rubber and thermoplastics, 2% for pharmaceuticals, and 15% for other uses. A small amount of lithium carbonate is recovered domestically through the recycling of lithium batteries (USGS, 2011).

The utilization of lithium in the battery industry has enormous growth potential. Both rechargeable and non-rechargeable lithium batteries are used in a variety of portable electronics and tools, while rechargeable lithium ion batteries are being developed for hybrid and electric vehicles. Most lithium minerals are used directly as ore concentrates, but lithium carbonate and lithium hydroxide are the prevalent battery feedstock materials.

Chile dominates the world lithium market. Other major producers of lithium compounds and ore concentrates include Argentina, China, Australia, Canada, Portugal, Zimbabwe, and the United States (USGS, 2011). Table 2 provides salient statistics from major global lithium producers.[2]

Domestically, only one company is currently producing lithium from U.S. soil. Chemetall Foote Corp., its sole operation a brine evaporation unit at Silver Peak, NV, does not disclose the quantities of lithium it produces. In 2010, the apparent domestic lithium consumption was 1,000 metric tons (USGS, 2011) but does not include consumption of imported batteries. The U.S. has nevertheless become the world leader in exporting downstream lithium compounds, which it produces domestically from imported carbonate, lithium hydroxide and lithium chloride. In the last decade, the U.S. has imported >50% of the lithium it consumed, but as of 2010 the net import reliance decreased to ~43% as a result of reduction in consumption due to the recent economic downturn. Not taken into account in these figures are direct battery imports, which are undoubtedly significant but not easily documented. Several companies have staked claims in Nevada to explore the potential of lithium-bearing aquifers but none have reached production phase (USGS, 2009).

Table 2. Global Lithium Production, Reserves and Resources (USGS, 2011).

Country	2010 Production (metric tons)	Reserves (metric tons)	Resources (metric tons)
United States	N/A	38,000	4,000,000
Argentina	2,900	850,000	2,600,000
Australia	8,500	580,000	630,000
Brazil	180	64,000	1,000,000
Canada	0	N/A	360,000
Chile	8,800	7,500,000	7,500,000
China	4,500	3,500,000	5,400,000
Potugal	0	10,000	N/A
Zimbabwe	470	23,000	N/A
Bolivia	N/A	N/A	9,000,000
Congo	N/A	N/A	1,000,000
Serbia	N/A	N/A	1,000,000
World Total	25,350	12,565,000	32,490,000

Conventional means of producing lithium include brine evaporation and hard-rock extraction from the mineral spodumene. Brine evaporation, by far the most common method, employs a process known as Lime Soda Evaporation in which subsurface brine is pumped into evaporation ponds. The brine is treated with lime and soda ash and over a period of 12 to 18 months evaporates so that lithium chloride and a variety of other salts crystallize (Tahil, 2007).

Spodumene, a lithium-bearing silicate with chemical formula $LiAlSi_2O_6$, is typically harvested from large pegmatite veins. In its purest form, spodume forms highly sought after pink and green gemstones (Mindat, 2011). Until 1997, most lithium carbonate produced was obtained from spodumene mining, but the entry of far-cheaper brine evaporation drove most spodumene mining operations out of the market (Tahil, 2007).

Despite their proven technologial feasibilities, these two methods introduce a variety of environmental concerns that could be eliminated through lithium extraction from geofluids. Large-scale evaporation requires immense swaths of land and long-term solar exposure, produces enormous quantities of waste salts, and introduces the question of water rights in areas of freshwater scarcity. Hard-rock spodumene mining is invasive and produces large quantities of mine waste. In the case of geofluid co-production, the only land use and disruption occur during the development of the power plant and drilling of injection/production wells, and water loss is minimal as produced fluid is reinjected into the reservoir after energy extraction and processing take place.

6. Lithium Ion Batteries in Electric Vehicles: A Growing Market

Lithium-ion batteries for use in electric vehicles (EVs) are a very promising contributor to reducing our dependence on imported oil. But is there enough lithium? Will we need to import it from a new and unfriendly cartel? The market for lithium is likely to be dominated by its use in batteries, as can be seen in Figure 1 (Anderson, 2011), and automotive batteries are by far the fastest-growing type. We explore the potential demand for lithium in vehicle batteries if hybrid vehicles like those on the road today, plug-in hybrids with different all-electric ranges, and pure electric vehicles expand their market share extremely rapidly. This is not a projection, but rather an upper bound on the quantity of material that could be required. The total demand is then compared to estimates of production and reserves, and quantities that could be recycled, to evaluate the adequacy of future supply.

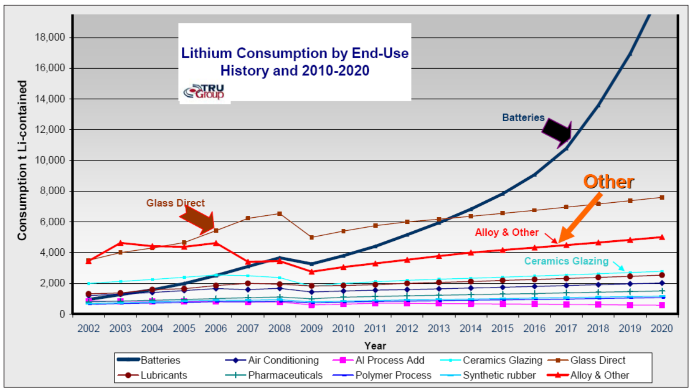

Figure 1. Batteries will dominate future lithium demand (borrowed with permission from TRU, 2011).

First, an estimate of total vehicle demand vs. time was combined with a scenario of percent of new sales by each technology vs. time to calculate the number of new vehicles of each type produced annually. To estimate U.S. sales of vehicles with some form of electric drive, we extended the Energy Information Administration (EIA) projections of light vehicle sales for the United States from 2030 (DOE/EIA, 2008) to 2050, using a model based on Gross Domestic Product, fuel price, and projections of driving-age population by using the VISION 2007 model (Argonne, 2008). We took the most optimistic scenario for penetration into the U.S. market from the DOE Multi-Path Study (Phase 1)(DOE, 2007). In this scenario, 90% of all light-duty vehicle sales are some type of electric vehicle by 2050. This represents the maximum percent of U.S. sales that could be accounted for by. Upper-bound world demand was also estimated. We relied on an IEA scenario (IEA, 2009) for world demand. IEA is developing scenarios of what would need to be done to meet IPCC CO_2-reduction goals. This scenario characterizes an aggressive adoption of many advanced technologies; about 1.6 billion electric-drive vehicles have been built by 2050 in this scenario, with pure EVs accounting for over 20% of global sales. This is a key assumption that would cause high lithium demand.

Batteries were designed for each vehicle type, the battery masses estimated, and the total annual lithium requirement calculated, assuming that all vehicles used the current NCA-Graphite chemistry. Finally, materials potentially available via recycling were estimated to determine net virgin material required, and compared to production and reserves. Table 3 (Gaines et al., 2010) shows how total cumulative world demand for lithium up to 2050 would compare to reserve estimates for the IEA scenario and a similar scenario using batteries a factor of 3 smaller, both recycled and not. The economic reserves would not be used up, and recycling could extend them significantly.

Table 3. World Lithium Demand and Reserves (Gaines et al., 2010).

	Cumulative demand to 2050 (Contained lithium, 1000 Metric tons)
Large batteries, no recycling	6,474
Smaller batteries, no recycling	2,791
Smaller batteries, recycling	1,981
	Reserve Estimates
USGS Reserves	9,900
USGS World Resource	25,500
Other Reserve Estimates	30,000+

One reason for increasing domestic US production of lithium would be to become less dependent on imported raw materials. Under our optimistic EV scenario, the US would require a total of about one million tons of lithium with no recycling, and about half that if all the material could be recycled after 10 years of use. The currently economic reserves in the US are 38,000 tons (USGS, 2011), clearly insufficient, but the total resource (available at higher cost) is about 4 million tons, which could eliminate our lithium imports. However, the price would need to be higher. How would that impact the cost of the vehicles that would be using the material in their batteries? The Chevrolet Volt and the Nissan Leaf, the 2 electric-drive vehicles now available in the US, contain about 2 kg and 4 kg of lithium in their battery packs, respectively. At the current market price of ~$5000/ton of lithium carbonate (Ehren, 2009), that raw material costs $50-$100 per vehicle. When this is compared to the vehicle prices of $30,000-$40,000, it is clear that even a doubling of the cost of lithium would not be a significant perturbation on the vehicle price. Therefore, a cost increase (if it were to happen) caused by using domestic suppliers could be tolerated by the vehicle market.

If 5,400 metric tons of lithium carbonate were produced annually from the Salton Sea, 250,000-500,000 cars using 2-4 kg of lithium could use this domestic resource for their batteries. At that rate, only 2-4 years' production would meet President Obama's one million vehicle goal.

7. Discussion

The advantages of co-produced lithium over conventional lithium production are manifold. If the electric vehicles industry is to expand as it has the potential to, and as President Obama has promised, the foreign dependence of our lithium supply chain cannot be overlooked. The U.S. possesses an abundance of lithium, but even the little that the U.S. consumes has the potential to be produced domestically, providing political, environmental and financial benefits to U.S. consumers and geothermal power developers.

The economic and scientific potential of co-production from geothermal brines has been abundantly demonstrated in scientific literature and in decades of on-site demonstrations. With the potential to provide at least 5,400 metric tons of lithium carbonate and over $28 million in gross revenues to a single 40MW plant in the many resource areas of the Imperial Valley, CA, the promise of this technology is clear. Combining this potential with the environmental responsibility of the technology and the promise of greater political stability as compared to conventional production methods, this technology will be a key player in the energy future of the United States.

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[1] Salton Sea and Brawley resources geographically lie within the broader Imperial Valley resource area and are commonly interchanged in the literature. For the sake of this paper, all three will be included within the broader term "Imperial Valley resource area."

[2] The USGS differentiates the terms *reserve* and *resource* on the following basis (USGS, 2011):

- Reserve: That part of the resource (sic) which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials; thus, terms such as "extractable reserves" and "recoverable reserves" are redundant and are not a part of this classification system.
- Resource: A concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth's crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible.