

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

ENERGYSOURCE MINERALS, LLC

Petitioner

v.

ALL AMERICAN LITHIUM LLC

Patent Owner

U.S. Patent No. 9,057,117

SELECTIVE RECOVERY OF MANGANESE AND ZINC

IPR2019-01605

**DECLARATION OF DARRELL L. GALLUP, PH.D.
IN SUPPORT OF PETITION FOR *INTER PARTES* REVIEW
OF U.S. PATENT NO. 9,057,117**

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I, Darrell L. Gallup, Ph.D., hereby declare the following:

I. INTRODUCTION

1. I have been retained by counsel for EnergySource Minerals, LLC (“Petitioner”) as an expert witness to offer testimony with respect to the subject matter at issue herein. I have been asked to provide my opinions about the state of the art of the technology described in the U.S. Patent 9,057,117, entitled “Selective Recovery of Manganese and Zinc”, by Stephen Harrison, *et al.*, filed April 30, 2013, and issued June 16, 2015 (the “‘117 patent” or the “Challenged Patent”). I also have been asked to provide my opinions with respect to the patentability of Claims 12-15 and 21 (the “Challenged Claims”) of the ‘117 patent in connection with the above-captioned *inter partes* review (“IPR”) proceeding. The following is my written report on these topics.

2. I understand that the ‘117 patent has been provided as EX 1001. I understand that the ‘117 patent claims priority to U.S. Provisional Patent Application No. 61/241,479 filed September 11, 2011.¹ For the purposes of this IPR, I assume the earliest possible priority date of the ‘117 patent is the September 11, 2011 filing date of the provisional application to which the ‘117 patent claims priority. I understand

¹ Because the ‘117 patent claims a priority date before March 16, 2013, all citations to 35 U.S.C. herein are to 35 U.S.C. *pre-AIA* unless otherwise noted.

that the ‘117 patent was issued to Simbol Inc. and subsequently assigned to Alger Alternative Energy LLC, which recently changed its name to All American Lithium LLC (“All American”, or “Patentee”, “Patent Owner”, or “P.O.”, hereinafter).

3. I have reviewed and am familiar with the specification and the claims of the ‘117 patent.

4. I have reviewed and am familiar with the file history of the ‘117 patent. I understand that the file history has been provided in this IPR proceeding as EX 1002.

5. A complete listing of additional materials considered and relied upon in preparation of my declaration is provided below. I have relied on these materials to varying degrees. Citations to these materials that appear below are meant to be exemplary but not exhaustive.

6. The ‘117 patent describes methods for selective recovery of manganese, lead, and zinc from geothermal brines. EX 1001, at Title and Abstract. I am familiar with the subject matter described in the ‘117 patent as of the earliest possible priority date of the ‘117 patent (*i.e.*, September 11, 2011).

II. QUALIFICATIONS AND COMPENSATION

7. My *curriculum vitae* documenting some of the details of my professional experience, publications, and related information is attached hereto as “Exhibit A” and incorporated herein.

8. By way of summary, I have a Ph.D. in inorganic chemistry and over forty (40) years of industry experience in production optimization for the wastewater treatment industry. I am an internationally recognized authority on oil / gas production, chemistry, flow assurance, geothermal energy production, water treatment and environmental processes.

9. I am currently employed as a senior process chemist for Thermochem, Inc., Santa Rosa, California, where my job duties include consulting on matters involving geothermal brine scale and corrosion problems.

10. I am a named inventor on sixty-two (62) U.S. patents and numerous foreign counterparts, with one U.S. patent pending. I have published ninety-four (94) technical papers and written five (5) book chapters. I am a member of the Society of Petroleum Engineers (“SPE”) Production Engineering Editorial Board. I have been a member of the Geothermics Advisory Board since 2007 and a past member of the Geothermics Editorial Board, 2000-2006. I am past Chairman of the National Association of Corrosion Engineers (“NACE”) Geothermal Committee, 1999–2005 and past Vice-chairman 2011-2015. I served as chairman of the International Quality & Productivity Center (IQPC) Europe Produced Water Management Conference (2003), and as the chairman of the IQPC South East Asia 2008 Produced Water Conference. I was also chairman *pro-tem* of the 33rd International Geological

Conference (IGC) geothermal session and a member of the SPE 2009 Scale Workshop committee.

11. My expertise qualifies me to do the type of analysis required in this IPR. Specifically, I have been involved in the design, implementation, testing, and analysis of geothermal energy production, water treatment and environmental processes for over forty (40) years. My work has included analysis and design of projects directly related to the subject matter of the '117 patent. For example, I have authored eleven (11) papers and made numerous presentations that deal with various aspects of treating Salton Sea geothermal brines, which are characterized as representative examples of brines suitable for processing by the methods of the '117 patent. I have also directed the development of numerous products related to treatment of water from subsurface sources.

12. My work on this IPR is being compensated at my standard hourly rate for my review and testimony in this matter. I am also being reimbursed for reasonable and customary expenses associated with my work and testimony in this investigation. My compensation is not contingent upon the outcome of this IPR or the specifics of my testimony.

13. My opinions are based on my years of education, research and experience, as well as my investigation and study of relevant materials. In forming my opinions, I have considered the materials I have identified in this Declaration.

14. I may also consider additional documents and information in forming any necessary opinions including documents that may not yet have been provided to me.

15. My analysis of the materials produced in this IPR is ongoing and I will continue to review any new material as it is provided. This Declaration represents only those opinions I have formed to date. I reserve the right to revise, supplement, and/or amend my opinions stated herein based on new information and on my continuing analysis of the materials already provided.

16. Based on my education, training, and experience, I am familiar with the technology which is the subject of the ‘117 patent, the cited references, and general U.S. Patent and Trademark Office practices and procedures.

III. BACKGROUND

17. I have been asked to provide my opinions with respect to certain matters associated with Claims 12-15 and 21 of the ‘117 patent.

18. In preparing this Declaration, I have reviewed the following documents, among others:

- a. The “Petition for *Inter Partes* Review of U.S. Patent 9,057,117” (the “Petition”), filed by Petitioner.
- b. U.S. Patent 9,057,117 (the ‘117 patent; EX 1001), including its written description, figures, and claims.
- c. The file history of the ‘117 patent (EX 1002).

- d. Maimoni, A., *A Cementation Process for Minerals Recovery from Salton Sea Geothermal Brines*, Lawrence Livermore Library, January 26, 1982 (“*Maimoni*”; EX 1004).
- e. Bourcier, *et al.*, *Recovery of Minerals and Metals from Geothermal Fluids*, 2003 SME Meeting, Feb. 24 – Feb. 26, 2003. (“*Bourcier*”; EX 1005).
- f. Christopher, *et al.*, *The Recovery and Separation of Mineral Values from Geothermal Brines* (contract HO144104, Hazen Research Inc.), United States Department of the Interior, Bureau of Mines, OFR 81-75, June 12, 1975, (“*Christopher*”; EX 1006).
- g. U.S. Patent No. 4,405,463, for “Process for Stabilizing Silica-Rich Geothermal Brine to Prevent Silica Scaling”, to Jost, *et al.*, filed November 4, 1981, and issued September 20, 1983 (“*Jost*”; EX 1007).
- h. U.S. Patent No. 4,016,075, for “Process for Removal of Silica From Geothermal Brine”, to Wilkins, *et al.*, filed March 17, 1975, and issued April 5, 1977 (“*Wilkins*”; EX 1008).
- i. U.S. Patent No. 6,517,701, for “Lead, Zinc, and Manganese Recovery from Aqueous Solutions”, to Geisler, filed August 14, 2001 and issued Feb. 11, 2003 (“*Geisler*”; EX 1009).

- j. U.S. Patent No. 5,358,700, for “Method of Extracting Zinc from Brines”, to Brown, *et al.*, filed October 5, 1992, and issued October 25, 1994 (“*Brown*”; EX 1010).
- k. U.S. Patent No. 6,458,184, for “Recovery of Zinc from Geothermal Brines”, to Featherstone, filed December 20, 2000, and issued October 1, 2002 (“*Featherstone I*”; EX 1011).
- l. U.S. Patent Publication No. 2003/0226761, for “Process for Producing Electrolytic Manganese Dioxide from Geothermal Brines”, to Featherstone, *et al.*, filed May 31, 2002, and published December 11, 2003 (“*Featherstone II*”; EX 1012).
- m. Any other documents not listed above but referenced in the text that follows.

19. I have been asked to offer my opinion with respect to the technology associated with, and obviousness of, certain of the claims of the ‘117 patent in view of prior art references provided by the Petitioner.

20. The inventors of the ‘117 patent purport to have invented a method of removing zinc and manganese from geothermal brines; however, beginning in the 1970’s, brines from the Salton Sea Known Geothermal Resource Area (“KGRA”) were extensively studied and reported by third parties for scaling and corrosion issues on injection pumps, piping, well tubulars, and injection well formations from

iron silicates and silica found in Salton Sea geothermal brines, and then investigated recovering metal values from the Salton Sea geothermal brines. For example, *Maimoni* (EX 1004), *Bourcier* (EX 1005), and *Christopher* (EX 1006) each disclose selectively removing silica and iron from geothermal brines before subsequent zinc, manganese and other mineral recovery from the brine. *Maimoni* (EX 1004), *Christopher* (EX 1006), *Jost* (EX 1007), *Wilkins* (EX 1008), and *Brown* (EX 1010) each disclose selective removal of iron and silica from geothermal brines. *Maimoni* (EX 1004) and *Christopher* (EX 1006) disclose recovery of zinc and manganese from geothermal brines using precipitation, and *Bourcier* (EX 1005), *Geisler* (EX 1009), *Brown* (EX 1010), *Featherstone I* (EX 1011), and *Featherstone II* (EX 1012) disclose recovery of zinc and manganese using solvent extraction/ion exchange processes. Further, the extracted manganese could be further processed to produce manganese dioxide and/or electrolytic manganese dioxide according to *Bourcier* and/or *Geisler* and/or *Featherstone II*.

IV. GUIDING LEGAL PRINCIPLES

a. Person of Ordinary Skill in the Art

21. Based on my education, training, and professional experience in the field of the Challenged Claims, I am familiar with the level of the abilities of a person of ordinary skill in the art (“POSITA”) at the time of the Challenged Claims. It is my understanding that earliest priority date of the ‘117 patent is September 11, 2011.

22. In my opinion, a POSITA relevant to the priority date of the '117 patent would have an undergraduate scientific or engineering degree in a relevant field (such as chemistry, chemical engineering or metallurgy), at least five years' experience in aqueous solutions that contains a substantial amount of dissolved metals, separation, extraction and filtration technologies, and/or related geothermal brine field and/or hydrometallurgy chemistries, or a graduate degree conferring similar expertise, and an understanding of the relevant principles of chemistry and chemical engineering and hydrometallurgy technology.

b. My Understanding of Anticipation/Novelty

23. I understand that if each and every element of a claim is disclosed in a single prior art reference, then the claimed invention is anticipated and not patentable under 35 U.S.C. §102. In order for the invention to be anticipated, each element of the claimed invention must be described or embodied, either expressly or inherently, in a single prior art reference. I also understand that a reference inherently discloses a claim limitation when that claim limitation is necessarily present in the reference. I also understand that a prior art reference must be enabling in order to anticipate a patent claim.

24. I also understand that under certain circumstances, multiple references may be used to prove anticipation, specifically to: (a) prove that the primary reference

contains an enabled disclosure, (b) explain the meaning of a term used in the primary reference, or (c) show that a characteristic not disclosed in the reference is inherent.

c. My Understanding of Obviousness

25. I understand that the following standards govern the determination of whether a claim in a patent is obvious. I have applied these standards in my evaluation of whether the Challenged Claims would have been considered obvious at the time of the earliest priority date of the Challenged Patent, which I understand is the September 11, 2011 filing date of U.S. Provisional Application No. 61/241,479. EX 1001, at 1.

26. I understand that even if a prior art reference fails to anticipate a patent claim, the claim may nonetheless be invalid as “obvious,” if the differences between the subject matter claimed and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a POSITA.

27. I have been informed that a claim can be obvious in light of a single prior art reference or multiple prior art references. To be obvious in light of a single prior art reference or multiple prior art references, there must be a reason to modify the single prior art reference, or combine two or more references, in order to achieve the claimed invention. This reason may come from a teaching, suggestion, or motivation to combine, or may come from the reference or references themselves, the

knowledge of a POSITA, or from the nature of the problem to be solved, and may be explicit or implicit from the prior art as a whole.

28. I have been informed that the combination of familiar elements according to known methods is likely to be obvious when it does no more than yield predictable results. I also understand it is improper to rely on hindsight in making the obviousness determination. I have also been advised that the common sense and ordinary creativity of one skilled in the art can be relevant to obviousness.

V. DISCUSSION OF THE ‘117 patent

a. Background of the Subject Matter Disclosed in the ‘117 patent.

29. The ‘117 patent discloses a method for selective recovery of manganese and zinc from geothermal brines. The method involves removing silica and iron from the brine, then removing the zinc and extracting the manganese from the substantially silica free brine, and then oxidizing the manganese and zinc to form precipitates thereof, recovering the manganese and zinc precipitates, solubilizing the manganese and zinc precipitates, purifying the manganese and zinc, and forming a manganese precipitate, and recovering the zinc by electrochemical means. EX 1001. Abstract.

30. The ‘117 patent issued from U.S. Patent Application No. 13/874,004 (the ‘004 Application) that was filed April 30, 2013, claiming priority to U.S. Provisional Application No. 61/241,479 filed September 11, 2009. *Id.*, at 1.

31. The patent lists two inventors: Stephen Harrison and Samaresh Mohanta. *Id.* The assignee on the face of the patent is identified as being Simbol Inc., Pleasanton, CA , but I understand the current owner of this patent to be All American Lithium LLC.

b. Summary of the Claimed Invention of the ‘117 patent.

32. It is my understanding that Claims 12-15 and 21 of the ‘117 patent have been challenged in this IPR.

33. With respect to the Challenged Claims, Claims 12-15 and 21 are directed toward methods for recovering zinc and manganese from a brine. (Claims 12 and 21, preamble, EX 1001).

34. The claimed steps generally require providing a brine and then “selectively removing silica and iron”, “removing zinc”, and “extracting manganese”. Claims 12 and 20 are reproduced below:

[12.0] A method for recovering zinc and manganese from a brine, the method comprising the steps of:

[12.1] providing a brine, said brine comprising manganese and zinc;

[12.2] selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc;

[12.3] removing the zinc from the substantially silica free brine;

[12.4] extracting manganese from the substantially silica free brine;

[12.5] oxidizing the manganese to produce a manganese dioxide precipitate; and

[12.6] recovering the manganese dioxide precipitate.

[21.0] A method for recovering zinc and manganese from a brine, the method comprising the steps of:

[21.1] providing a brine, said brine comprising manganese and zinc;

[22.2] selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc;

[23.3] removing the zinc from the substantially silica free brine;

[24.4] extracting manganese from the substantially silica free brine

35. Dependent Claims 13-15 of the '117 patent further limit Claim 12.

VI. CLAIM CONSTRUCTION

36. I understand that claim construction in an *inter partes* review is now controlled by the standard in *Phillips v. AWH Corp.*, 415 F.3d 1303 (Fed. Cir. 2005) (*en banc*).

37. For example, claim construction begins with the language of the claims. *Id.*, at 1312-14. The “words of a claim are generally given their ordinary and customary meaning,” which is “the meaning that the term would have to POSITA in question at the time of the invention, *i.e.*, as of the effective filing date of the patent application.” *Id.*, at 1312-13. The specification is “the single best guide to the meaning of a disputed term and ... acts as a dictionary when it expressly defines terms used in the claims or when it defines terms by implication.” *Id.*, at 1321 (internal quotation marks omitted). Although the prosecution history “often lacks

the clarity of the specification and thus is less useful for claim construction purposes,” it is another source of intrinsic evidence that can “inform the meaning of the claim language by demonstrating how the inventor understood the invention and whether the inventor limited the invention in the course of prosecution, making the claim scope narrower than it would otherwise be.” *Id.*, at 1317.

38. Extrinsic evidence, such as expert testimony and dictionaries, may be useful in educating the court regarding the field of the invention or helping determine what a POSITA would understand claim terms to mean. *Id.*, at 1318-19. However, extrinsic evidence in general is viewed as less reliable than intrinsic evidence. *Id.*

39. I understand that in this proceeding, any claim term that is not construed should be given its plain and ordinary meaning.

a. “brine”

40. In the “Definitions” section of the ‘117 patent, the term “brine” is defined as follows:

As used herein, “**brine**” or “brine solution” refers to any aqueous solution that contains a substantial amount of dissolved metals, such as alkali and/or alkaline earth metal salt(s) in water, wherein the concentration of salts can vary from trace amounts up to the point of saturation. As used herein, **brine** refers to both geothermal brines and waste or by product streams from industrial processes.

EX 1001, 5:50-56, emphasis added.

41. Examples of brines are given as:

Generally, brines suitable for the methods described herein are aqueous solutions that may include alkali metal or alkaline earth chlorides, bromides, sulfates, hydroxides, nitrates, and the like, as well as natural brines. ... Brines can be obtained from natural sources, such as, Chilean brines or Salton Sea brines, geothermal brines, sea water, mineral brines (e.g., lithium chloride or potassium chloride brines), alkali metal salt brines, and industrial brines, for example, industrial brines recovered from ore leaching, mineral dressing, and the like. The method is also equally applicable to artificially prepared brine or salt solutions.

Id., 5:57-6:7.

42. It is my understanding that when the specification of a patent contains a definition of a particular term, generally that definition should be adopted in construing the claims of that patent.

43. The term “geothermal brine” is not defined in the specification of the ‘117 patent except as a type “brine” (*e.g.*, “As used herein, brine refers to both geothermal brines and waste or by product streams from industrial processes.” *Id.*, 5:54-56), but many examples are given in the ‘117 patent, including geothermal brines found in the Salton Sea. *Id.*, 6:1-2.

44. As such, a POSITA at the time of the invention would have understood the term “brine” to be a hot concentrated saline solution that has circulated through crustal rocks in an area of anomalously high heat flow and become enriched in substances leached from those rocks, such as those found in the Salton Sea and Chilean brines.

b. “selectively removing silica and iron”

45. Claims 12 and 21 includes the phrase “selectively removing silica and iron” from a geothermal brine as a claim limitation. This phrase is not defined in the ‘117 patent.

46. The ‘117 patent acknowledges that “[t]he removal of silica is an important step as the presence of silica can interfere with subsequent processes for the recovery of various other metals.” EX 1001, 6:18-20.

47. The ‘117 patent teaches that silica and iron are selectively removed from a brine solution by controlling the pH of the brine and oxidizing iron (II) to iron (III) such that the silica attaches to the iron (III) hydroxide to form a precipitate. *Id.*, 6:27-7:18. For example, in Figures 1-11 of the ‘117 patent, silica and iron are selectively removed from the geothermal brine by precipitation.

48. The ‘117 patent provides that the iron (II) in the brine is oxidized to iron (III) hydroxide by sparging the reaction vessel with air (*Id.*, 7:35-50) or by adding an oxidant, such as hypohalite compound. *Id.*, 7:51-63. A base (*e.g.*, calcium hydroxide or lime) is also added to control the pH of the solution between 4.5 and 6. *Id.*, 6:46-50.

49. Like the embodiments illustrated in Figures 1-11, Examples 1-3 of the ‘117 patent precipitate or selectively remove iron and silica from a synthetic brine by oxidizing the iron (II) to iron (III) using air and controlling the pH with the addition of a slurry of calcium hydroxide. *Id.*, 16:55-18:7.

50. The ‘117 patent goes on to note:

It will be recognized by those skilled in the art that iron (III) hydroxide may also have a significant affinity for arsenic (III) and (V) oxyanions, **and these anions, if present in the brine, may be co-deposited with the silica on the iron (III) hydroxide.**

Id., 6:59-63, emphasis added.

51. The ‘117 patent further acknowledges that “depending upon the pH of the solution, a lead precipitate may also be formed.” *Id.*, 7:28-30.

52. A POSITA would recognize that the process of selective removal of silica and iron disclosed above will coprecipitate silica and iron but would also necessarily coprecipitate at least some other metals and/or ions including, for example, arsenic and lead, if such were present in the brine.

53. As such and for purpose of construction of this phrase as used in the ‘117 patent, Petitioner proposes that the phrase “selectively removing silica and iron” from a brine should be construed to mean selectively precipitating silica and iron from the brine; however, a processing step that is intended to “selectively remove silica and iron” does not exclude the possibility that other metals and/or ions in the brine may be removed as well.

c. “substantially silica free brine”

54. Claims 12 and 21 include the requirement that after the silica and iron are selectively removed, a “substantially silica free brine” is produced. This phrase is not defined in the ‘117 patent.

55. One embodiment of the invention suggests that if at least about 80% of the silica present in the brine is removed, that would qualify as “substantially silica free”.

In explaining the process of Figure 1, the ‘117 patent states as follows:

One preferred method for the selective removal of silica and iron includes contacting the solution with iron (III) hydroxide at a pH of between about 4.5 and 6, preferably between about 4.75 and 5.5, more preferably between about 4.9 and 5.3. ...

The iron (III) hydroxide contacts the silica present in the brine and forms a precipitate. Without being bound to any specific theory, it is believed that the silica or silicon containing compound attaches to the iron (III) hydroxide. In certain embodiments, the ratio of iron (III) to silica is at least about 1:1, more preferably at least about 4:1. **The reaction of the iron (III) hydroxide with silica is capable of removing at least about 80% of the silica present, preferably at least about 90%, and more preferably at least about 95%, and typically depends upon the amount of iron (III) hydroxide present in the solution.**

Id., 6:17-21; 6:22-24; 7:3-13, emphasis added.

56. In the Examples section, a synthetic brine was sparged with air to oxidize the iron and a slurry of calcium hydroxide was added to control the pH of the brine. Based on the processing conditions disclosed, the ‘117 patent reports between 88.5% and 99.9% silica removal in connection with Examples 1-3. *Id.*, 16:55-18:7.

57. Because the amount of iron remaining in the brine after the selective removal of silica and iron is not a stated limitation of independent Claim 12, the resulting brine need not be substantially free of iron or other minerals and metals.

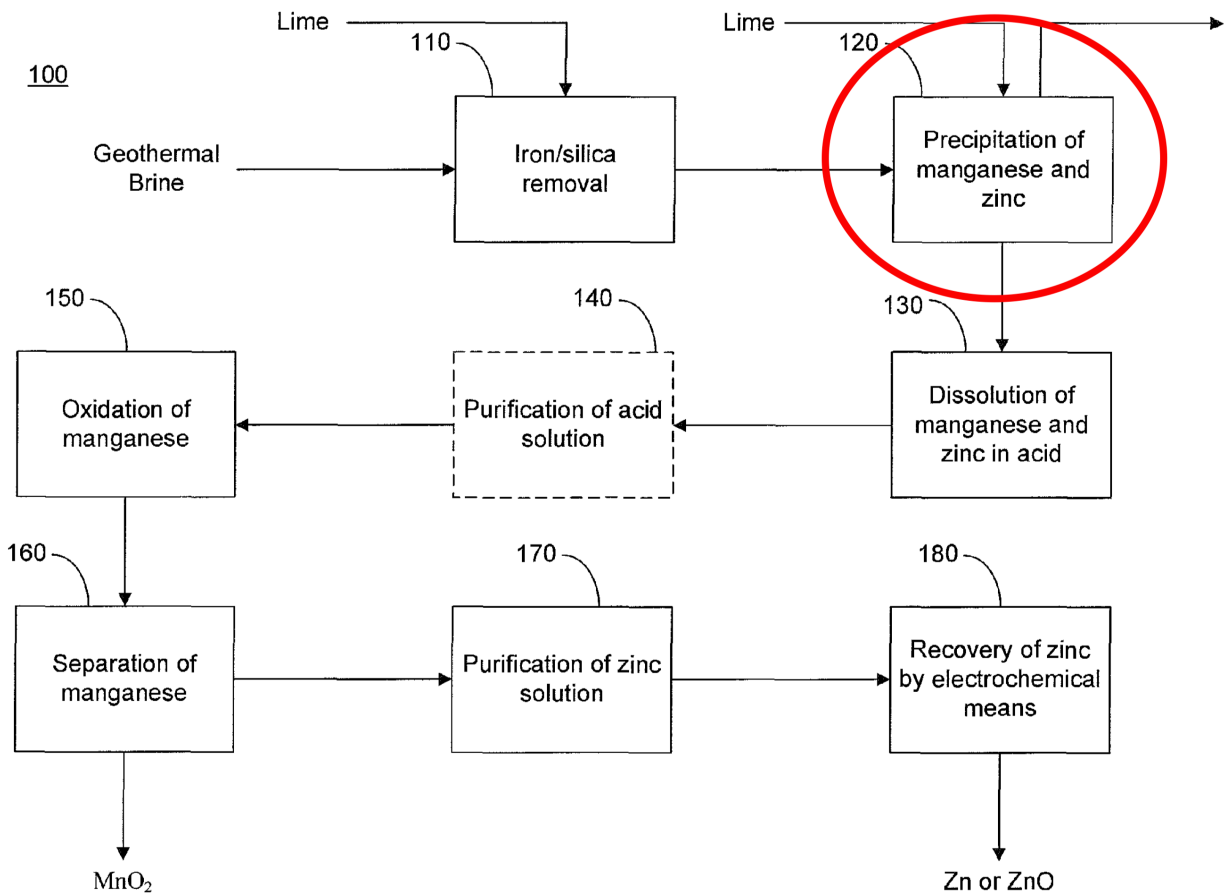
58. Accordingly, and for purposes construction of this term as used in the ‘117 patent, based on my review of the ‘117 patent I believe the phrase “substantially silica free brine” should be construed to mean a brine having a concentration of silica reduced by at least about 80% relative to the feed brine.

d. “removing the zinc”

59. Claims 12 and 21 include the phrase “removing the zinc” as part of this claim limitation. The phrase “removing the zinc” is not defined in the ‘117 patent.

60. Based on my review of the ‘117 patent and other documents described below, it is my professional opinion that the phrase “removing the zinc” as it is used in the ‘117 patent should be construed as removing or separating zinc from a geothermal brine by precipitation, solvent extraction or ion exchange.

61. The ‘117 patent teaches that after iron and silica removal, zinc can be removed from the substantially silica and iron free brine by precipitation. For example, in Figures 1 and 4-11 of the ‘117 patent, zinc is *removed* from the geothermal brine by precipitation. Exemplary Figure 1 is shown below:



Id., at Figure 1, highlighting added.

62. The '117 patent states that with respect to box 120:

After silica and iron removal step 110, **in precipitation step 120**, a base (e.g., calcium oxide, calcium hydroxide or the like) is added to the brine to adjust or maintain a pH of the brine at greater than at least about 6, alternatively between about 6 and 8.5, alternatively between about 6.5 and 8, alternatively between about 6.5 and 7.5. ... Furthermore, the solution is exposed to an oxygen source and manganese and **zinc precipitates are formed**.

...

The solids in the brine and base, which solids can include at least manganese and zinc, are separated from the remainder of the mixture, which retains the majority of ions present in the brine. Separation of the solids can be done by conventional filtration means and can optionally

include centrifugation or other known techniques for concentration the solids. In certain embodiments, the remaining brine solution from which the manganese and **zinc** have been **removed** can then be reinjected into the geothermal well from which the brine was originally **removed**.

Id., 7:14-38, emphasis added.

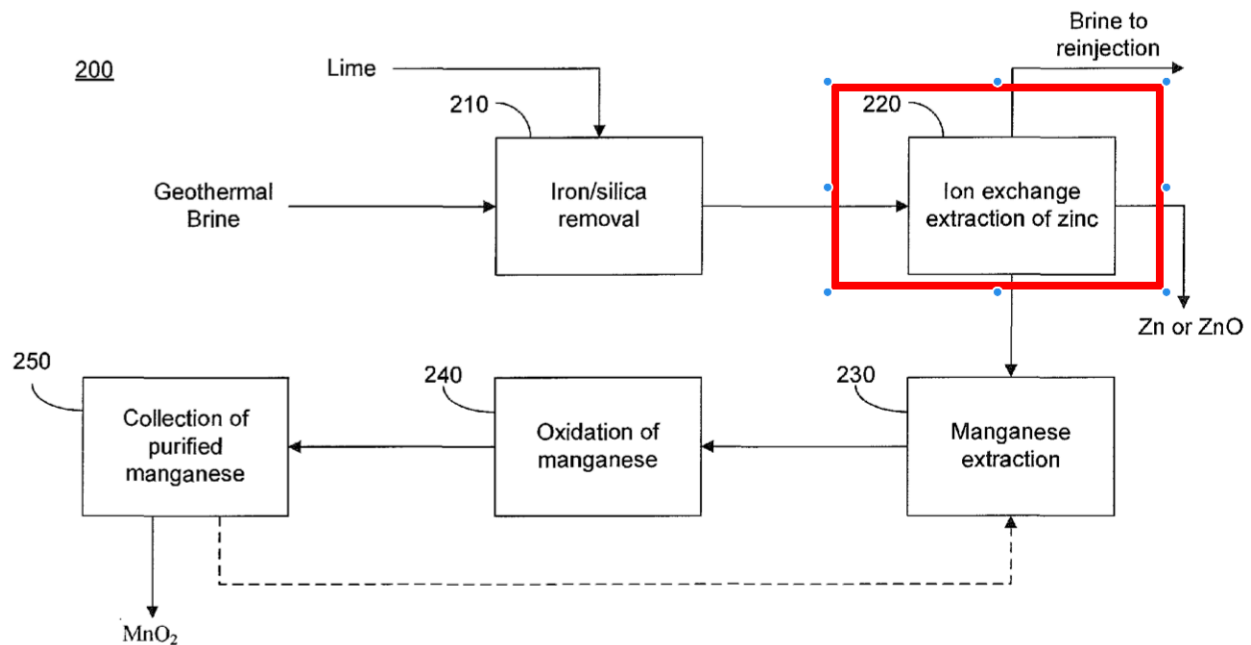
63. Similar to the precipitation step 120, the ‘117 patent coprecipitates zinc and manganese from the brine in “precipitation step[s]” 420, 520, 620, 720, 820, 920, 1020 and 1120 after the removal of silica and iron. *Id.*, 11:50-16:7; Figures 4-11.

64. Examples 4 and 5 of the ‘117 patent precipitate zinc from a synthetic brine having no reported silica and 0.8 mg/L (Example 4) and 0.3 mg/L (Example 5) of iron. *Id.*, 18:9-48. In these two Examples, the synthetic brine was sparged with air to oxidize the iron and a slurry of calcium hydroxide was added to control the pH of the brine. Based on the processing conditions disclosed, the ‘117 patent reports that 94.6% of the zinc was removed in Example 4, but contained “about 75% of the iron present in the brine. Due to the high recovery of iron by this process, the need for removal is confirmed.” *Id.*, 18:26-28.

65. In Example 5, the iron concentration in the synthetic brine was decreased (*e.g.*, to 0.3 mg/L from 0.8 mg/L) and the pH of the brine was modified in comparison to Example 4. Based on these modified processing conditions, the ‘117 patent reports that about 99.9% of the zinc was removed from the brine. *Id.*, 18:30-48.

66. Thus, based on my review of the ‘117 patent, in my professional opinion the term “remove” as used in this patent as applied to zinc includes removing or separating zinc from the geothermal brine by precipitation.

67. The ‘117 patent also teaches a “zinc *removal* process **220** that can include an ion exchange process.” *Id.*, 10:30-31.



Id., Figure 2, highlighting added.

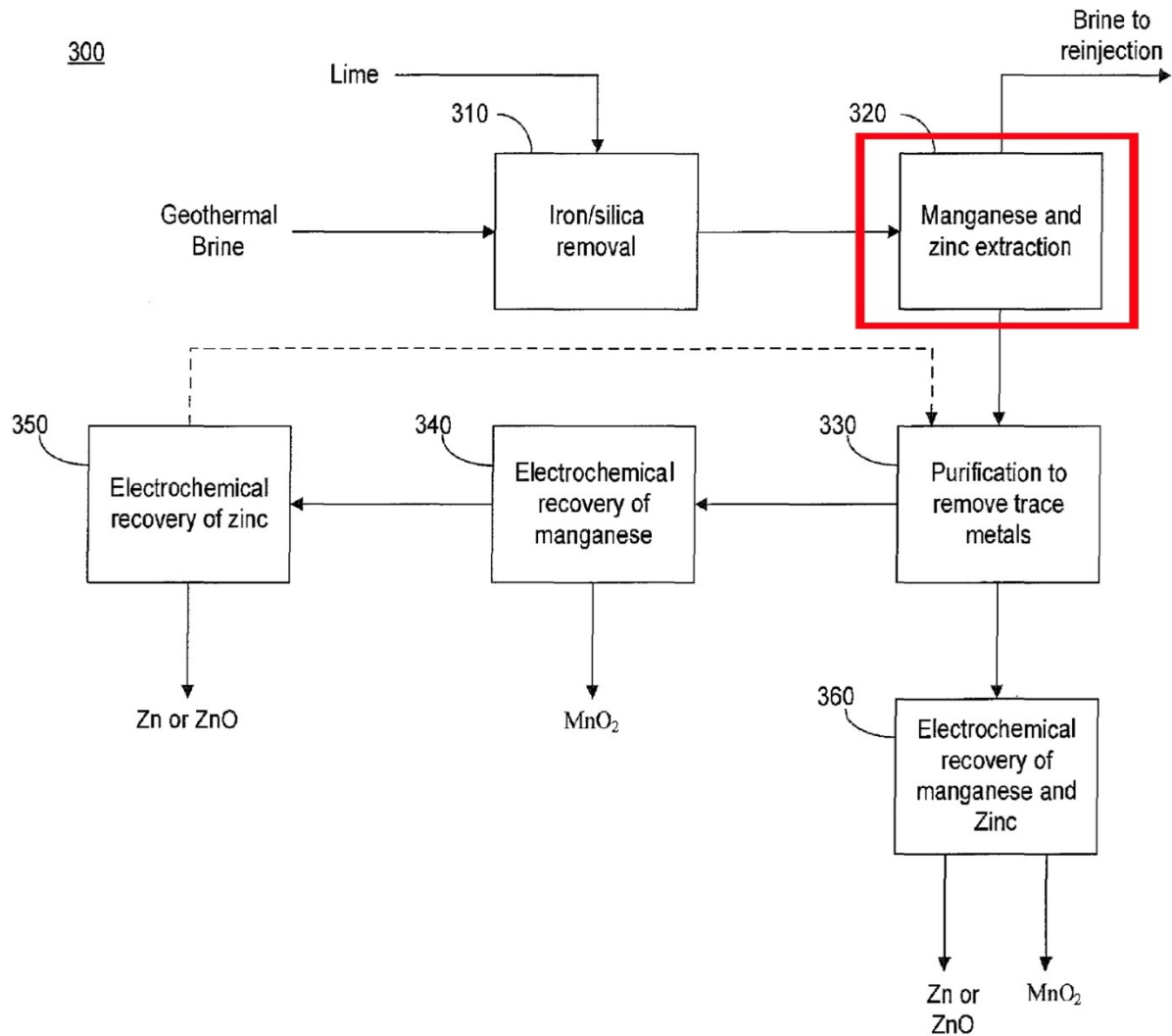
68. The ‘117 patent provides additional details of Step 220.

The brine solution, now having a reduced concentration of silica and iron relative to the initial brine feed, **can be supplied to zinc removal process 220 that can include an ion exchange process**, for example a basic anionic ion exchange resin like the chloride of a quaternary amine divinylbenzene/styrene copolymer, or the chloride of trimethylamine functionalized chloromethylated copolymer of styrene and divinylbenzene, such as is described in U. S. Pat. Nos. 6,458,184 [*Featherstone I EX 1011*], which is incorporated herein by reference in its entirety.

Id., 10:28-37, emphasis added. *Accord*: “In a second embodiment, ... **removing the zinc** from the substantially silica free brine by means of an **ion exchange** or other process”, *Id.*, 2:15-22, emphasis added.

69. Thus, based on my review of the ‘117 patent, in my professional opinion the term “remove” as used in this patent as applied to zinc includes removing or separating zinc from the geothermal brine by ion exchange.

70. In another example and in connection with the process illustrated in Figure 3 (reproduced below), “manganese and zinc can be *removed* by liquid-liquid extraction step 320”, emphasis added. *Id.*, 11:4-6. “Exemplary liquids suitable for extraction of manganese and zinc are described in U.S. Pat. No. 6,458,184 [*Featherstone I* EX 1011] and U.S. Pub. Pat. App. No. 20030226761 [*Featherstone II* EX 1012], the disclosures of which are incorporated herein by reference in their entirety. The solvents can include, for example, water-immiscible cationic organic solvents, such as di-2-ethyl-hexyl phosphoric acid (D2EHPA), or other similar solvents, as known in the art.” *Id.*, 11:6-13.



Id., at Figure 3, highlighting added.

71. The '117 patent provides that suitable solvents for the extraction of zinc include:

phosphines, phosphoric acids, and phosphinic acids, such as the following: di(2-ethylhexyl)phosphoric acid (DEHPA) in kerosene or Cyanex® 272 (bis(2,4,4-trimethylpentyl)phosphinic acid); Ionquest 290 (available from Rhodia Inc.) in aliphatic kerosene or the highly branched carboxylic acid extractant (versatic 10)(10-decyl-4-pyridinecarboxylate). In certain embodiments, DEHPA is a suitable extraction solvent, particularly in embodiments where iron has been previously removed.

Other exemplary solvents that may be used for the extraction of zinc are discussed in U.S. Pat. No. 5,135,652, the disclosure of which is herein incorporated by reference in its entirety. These exemplary solvents include mono-2-ethylhexylphosphoric acid (M2EHPA), di-2-ethylhexylphosphoric acid (D2EHPA), and mixtures thereof (EHPA). Other exemplary solvents include bis-2,4,4-trimethylpentylmonothiophosphinic acid (Cyanex® 302) and bis-2,4,4-trimethylpentyldithiophosphinic acid (Cyanex® 301). In certain embodiments, the extractant includes both phosphoric acid and phosphinic acid...

...

Other solvents suitable for the extraction of zinc from brine solutions are described in “Recovery of Zinc(II) from Acidic Sulfate Solutions. Simulation of Counter-Current Extraction Stripping Process”, Gotfryd, L. and Szymanowski, J.; Physicochemical Problems of Mineral Processing, vol. 38 (2004), pp. 113-120; “New Developments in the Boleo Copper-Cobalt-Zinc-Manganese Project”, Dreisinger, et al.; available at http://bajamining.com/_resources/Reports/alta_paper—2006_boleo_final.pdf; “Zinc Solvent Extraction in the Process Industries”, Cole, P. and Sole, K.; Mineral Processing and Extractive Metallurgy Review, vol. 24, no. 2 (2003), pp. 91-137; “Solvent extraction of zinc(II) and manganese(II) with 5,10,15,20-tetraphenyl-21H,23H-porphine(TPP) through the metal exchange reaction of lead(II)-TPP”, Kawai, T., Fujiyoshi, R., and Sawamura, S.; Solvent Extr. Res. Dev. Japan, vol. 7 (2000), pp. 36-43, “Solvent Extraction of Zinc from Strong Hydrochloric Acid Solution with Alamine336”, Lee, M. and Nam, S.; Bull. Korean Chem. Soc., vol. 30, no. 7 (2009), pp. 1526-1530, the disclosures of which are incorporated herein by reference.

Id., 8:14-61.

72. Based on my review of the ‘117 patent, in my professional opinion the term “remove” as used in this patent as applied to zinc includes removing or separating zinc from the geothermal brine by solvent extraction.

73. As such, in my professional opinion the phrase “removing the zinc” in the context of Claims 12 and 21 of the ‘117 patent includes removing or separating zinc from the geothermal brine by precipitation, solvent extraction or ion exchange.

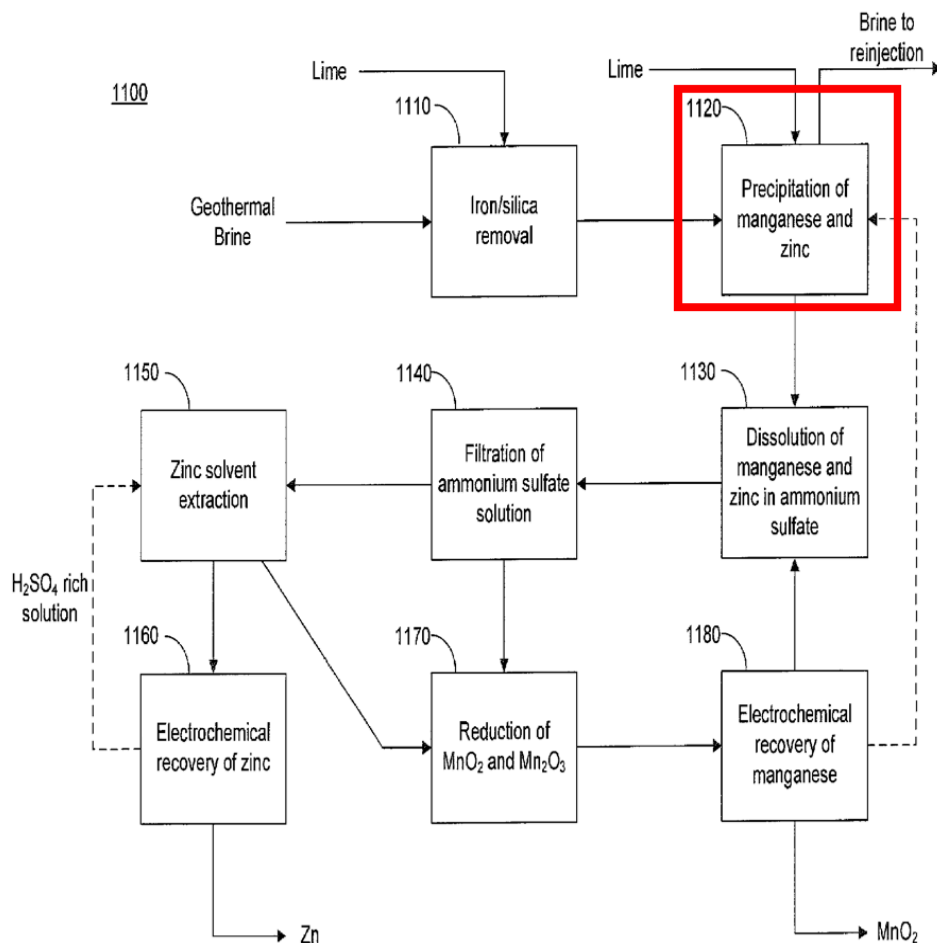
74. Thus, in my professional opinion the phrase “removing the zinc” in the context of Claims 12 and 21 of the ‘117 patent should be construed as removing or separating zinc from the geothermal brine by precipitation, solvent extraction or ion exchange.

e. “extracting manganese”

75. Claim 12 includes the phrase “extracting manganese” as part of a claim limitation. The phrase “extracting manganese” is not defined in the ‘117 patent.

76. Based on my review of the ‘117 patent and other documents described below, it is my professional opinion that the phrase “extracting manganese” as it is used in the ‘117 patent, like the term “removing the zinc” discussed *infra*, should be construed as extracting or separating manganese from a geothermal brine by precipitation, solvent extraction or ion exchange.

77. The ‘117 patent teaches that extraction of manganese can include extracting by precipitation. For Example, in Figures 1 and 4-11 of the ‘117 patent, manganese is *extracted* from the geothermal brine by precipitation. Exemplary Figure 11 is shown below:



EX 1001, at Figure 11, highlighting added. “In certain embodiments, the remaining brine solution from **extraction step 1120, from which the manganese and zinc have been removed**, can then be reinjected into the geothermal well from which the brine was originally removed.” *Id.*, 16:13-17, emphasis added.

78. The ‘117 patent teaches that:

After silica and iron removal step 110, **in precipitation step 120**, a base (e.g., calcium oxide, calcium hydroxide or the like) is added to the brine to adjust or maintain a pH of the brine at greater than at least about 6, alternatively between about 6 and 8.5, alternatively between about 6.5 and 8, alternatively between about 6.5 and 7.5. ... Furthermore, the

solution is exposed to an oxygen source and **manganese** and zinc **precipitates are formed**.

...

The solids in the brine and base, which solids can include at least manganese and zinc, are separated from the remainder of the mixture, which retains the majority of ions present in the brine. Separation of the solids can be done by conventional filtration means and can optionally include centrifugation or other known techniques for concentration the solids. In certain embodiments, the remaining brine solution from which the **manganese** and zinc have been **removed** can then be reinjected into the geothermal well from which the brine was originally **removed**.

Id., 7:19-26; 8:34-43, emphasis added.

79. Similar to the precipitation step 1120, the ‘117 patent coprecipitates zinc and manganese in “precipitation step” 120, 420, 520, 620, 720, 820, 920, and 1020 after the removal of silica and iron. *Id.*, 6:13-15:65; Figures 4-11.

80. Examples 4 and 5 of the ‘117 patent precipitate manganese from a synthetic brine having no reported silica and 0.8 mg/L (Example 4) and 0.3 mg/L (Example 5) of iron. *Id.*, 18:8-48. In the two Examples, the synthetic brine was sparged with air to oxidize the iron and a slurry of calcium hydroxide was added to control the pH of the brine. Based on the processing conditions disclosed, the ‘117 patent reports that 95.2% of manganese was extracted in Example 4, but contained “about 75% of the iron present in the brine. Due to the high recovery of iron by this process, the need for removal is confirmed.” *Id.*, 18:26-28.

81. In Example 5, the iron concentration in the synthetic brine was decreased (*e.g.*, to 0.3 mg/L from 0.8 mg/L) and the pH of the brine was modified in comparison to Example 4. “A precipitate was collected which included zinc and manganese.” *Id.*, 18:39-40. Based on these modified processing conditions, the ‘117 patent reports that about 100% of the manganese was removed from the brine by precipitation. *Id.*, 18:47-48.

82. Thus, based on my review of the ‘117 patent, in my professional opinion the phrase “extracting manganese” includes extracting or separating manganese from the geothermal brine by precipitation.

83. In addition, the text associated with Step 230 indicates that manganese can be extracted by “ion exchange, solvent extraction, or like process”:

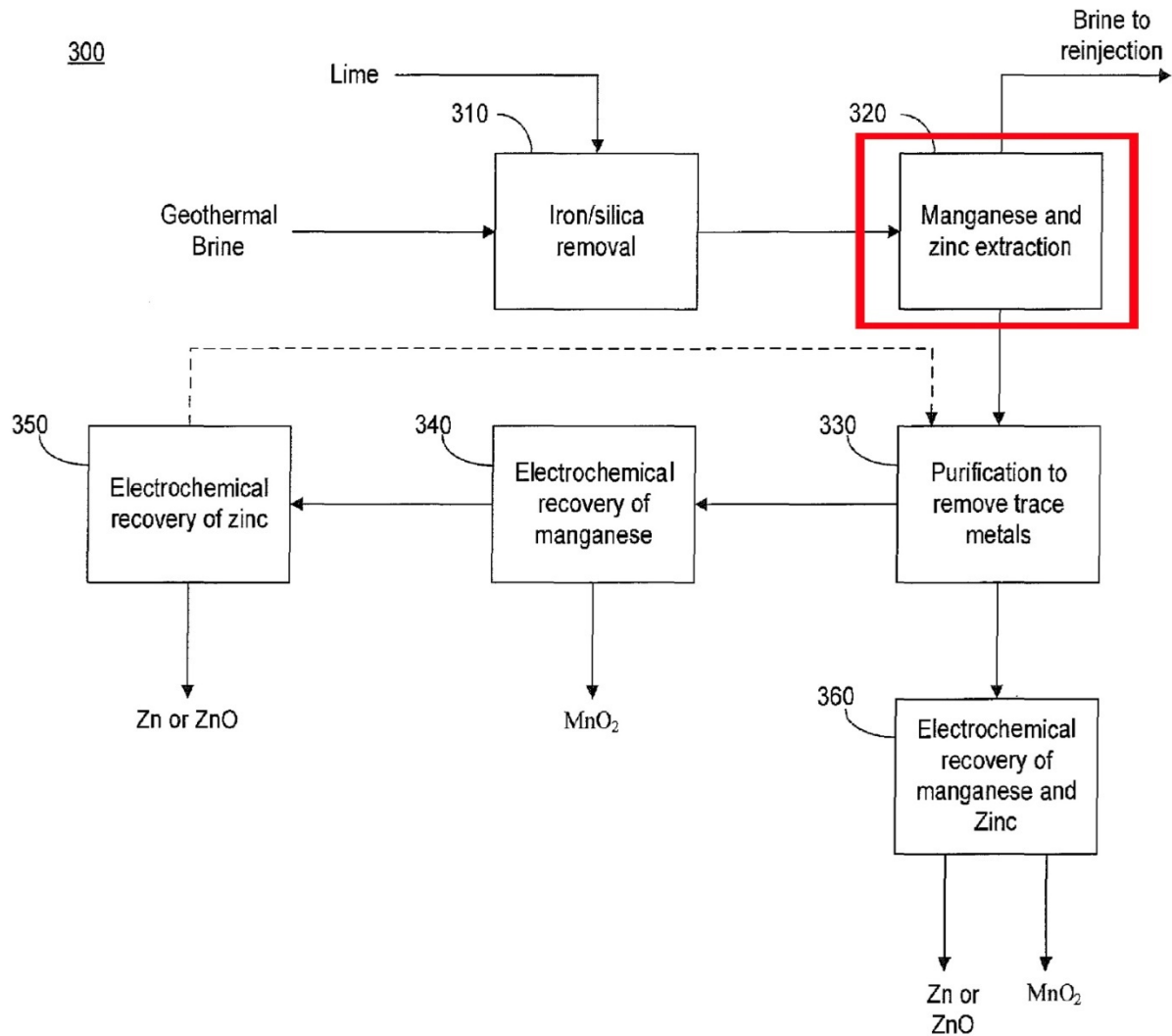
The remaining solution, which includes manganese, can then optionally be supplied to **purification step 230 and purified by ion exchange, solvent extraction, or like process**, and the manganese containing phase can be provided to oxidation step **240**, such as an electrochemical cell or chemical oxidation process, as described with respect to FIG. 1, to facilitate the recovery of manganese dioxide.

Id., 10:45-51, emphasis added. *Accord*: “The fifth embodiment can further include ... **extracting manganese by solvent extraction** and then recovering manganese”.

Id., 2:62-3:8, emphasis added.

84. As such, it is my professional opinion that “extracting manganese” includes extracting or separating manganese from a geothermal brine by solvent extraction or ion exchange.

85. Similar to the zinc removal step discussed above, in another example and in connection with the process of Figure 3 (see below), “manganese and zinc can be *removed* by liquid-liquid extraction step 320”. *Id.*, 11:5-6. In this embodiment exemplified in Figure 3, manganese is removed directly from the clarified brine using liquid-liquid extraction (*i.e.*, solvent extraction). *Id.*, 11:18-44. As discussed above in relation to “removing the zinc”, the ‘117 patent states that manganese can be extracted from a silica free brine by solvent extraction using [*Featherstone I* EX 1011], [*Featherstone II* EX 1012], and “water-immiscible cationic organic solvents, such as di-2-ethyl-hexyl phosphoric acid (D2EHPA), or other similar solvents, as known in the art.” *Id.*, 11:10-13.



Id., at Figure 3, highlighting added.

86. The '117 patent provides that suitable solvents for the extraction of manganese include:

phosphines, phosphoric acids, and phosphinic acids, such as the following: di(2-ethylhexyl)phosphoric acid (DEHPA) in kerosene or Cyanex® 272 (bis(2,4,4-trimethylpentyl)phosphinic acid); Ionquest 290 (available from Rhodia Inc.) in aliphatic kerosene or the highly branched carboxylic acid extractant (versatic 10)(10-decyl-4-pyridinecarboxylate). In certain embodiments, DEHPA is a suitable extraction solvent, particularly in embodiments where iron has been previously removed.

Id., 8:14-22.

87. Thus, based on my review of the ‘117 patent, in my professional opinion the term “extracting” as used in this patent as applied to manganese includes extracting or separating manganese from the geothermal brine by solvent extraction.

88. Based on my review of the ‘117 patent, in my professional opinion the phrase “extracting manganese” as used in the ‘117 patent should be construed as extracting or separating manganese from the geothermal brine by precipitation, solvent extraction or ion exchange.

f. “oxidizing the manganese”

89. Claim 12 includes the phrase “oxidizing the manganese”, but that phrase is not defined in the ‘117 patent.

90. The ‘117 patent teaches that oxidizing the manganese by chemical oxidation. For example, in Figure 1-2 and 5-6 of the ‘117 patent, manganese is oxidized by chemical oxidation to produce a manganese dioxide precipitate. Exemplary Figure 1 is shown below:

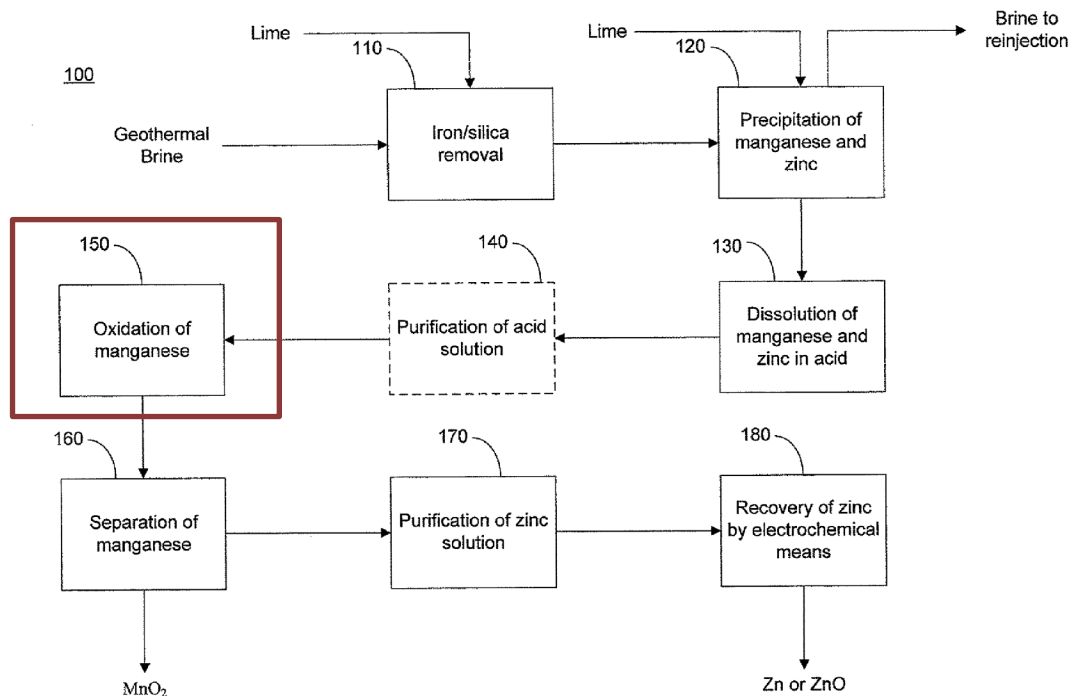


Figure 1

EX 1001, Figure 1, highlighting added.

91. The ‘117 patent teaches:

Manganese can be isolated by electrolysis or, in step 150, by oxidation to produce manganese dioxide, or by precipitation as a carbonate by reaction with sodium carbonate. ... Alternatively, selective oxidation of manganese to manganese dioxide can be achieved utilizing an oxidant, such as chlorine, hydrogen peroxide, or the like to provide solid manganese dioxide and zinc containing solution.

Id., 8:62-9:4, emphasis added.

92. Similar to the chemical oxidation step 150, the ‘117 patent chemically oxidizes manganese in “oxidation step” 240, 550, and 680 after the removal of silica

and iron. *Id.*, 10:45-52; 12:46-49; 13:15-17; Figures 2, 5-6. Precipitated manganese dioxide is then recovered or separated in by known means, such as filtration, centrifugation, or a like process. *Id.*

93. Thus, based on my review of the ‘117 patent, in my professional opinion the phrase “oxidizing the manganese” includes oxidizing the manganese by chemical oxidation.

94. In addition, the ‘117 patent discloses that manganese can be oxidized by electrolysis at an anode in an electrochemical cell to produce a manganese dioxide precipitate. *Id.*, 8:64-67. “[M]anganese dioxide can be generated at the anode of a divided electrochemical cell by the oxidation of manganese (II) and manganese (III) to generate a manganese dioxide deposited on the surface of the electrode.” *Id.*, 9:8-12. The ‘117 patent notes that “it may be advantageous to remove solid manganese dioxide from the electrolytic stream formed in the anode compartment that may be lost from the surface of the anode, such as by filtration, prior to supplying to the cathode compartment.” *Id.*, 9:20-24.

95. “[T]he manganese containing phase can be provided to oxidation step 240, such as an electrochemical cell or chemical oxidation process, as described with respect to FIG. 1, to facilitate the recovery of manganese dioxide. Purified manganese can be collected in step 250 by filtration.” *Id.*, 10:48-51. Similarly,

Figures 2-4 and 7 of the '117 patent illustrate manganese being electrochemically oxidized to produce a manganese dioxide precipitate. Figure 4 is shown below:

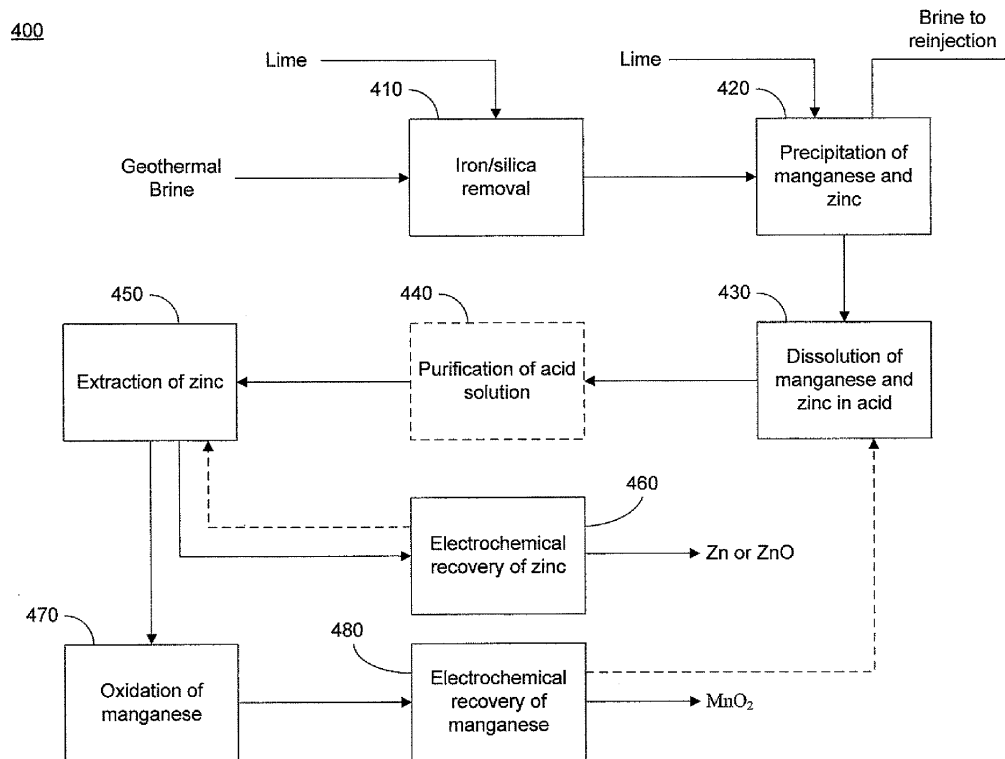


Figure 4

Id., at Figure 4.

96. “Manganese can be recovered by first oxidizing the manganese in step 470 to produce manganese dioxide, as previously discussed, which can then be recovered electrochemically in step 480 by known means.” *Id.*, 12:15-18. Similarly, “[i]n step 960, manganese can be recovered from the solution by electrolytically depositing manganese dioxide from the substantially silica free brine, such as by electrowinning or a like process.” *Id.*, 14:67-15:3.

97. Thus, based on my review of the ‘117 patent, in my professional opinion the phrase “oxidizing the manganese” includes electrochemically oxidizing the manganese to produce a manganese dioxide precipitate at the anode of an electrochemical cell.

98. Based on my review of the ‘117 patent, in my professional opinion the phrase “oxidizing the manganese” should be construed as oxidizing the manganese to produce manganese dioxide precipitate by chemical oxidation or electrochemical oxidation by electrowinning at the anode of an electrochemical cell.

g. “recovering the manganese dioxide precipitate”

99. Claim 12 of the ‘117 patent includes the phrase “recovering the manganese dioxide precipitate”, but that phrase is not defined in the ‘117 patent.

100. The ‘117 patent provides that after manganese is oxidized to produce manganese dioxide precipitate, the manganese dioxide precipitate is then recovered or separated in steps 160, 250, 480, 560, 680 by “**known means**,” such as filtration, centrifugation, electrochemically or a like process. *Id.*, 9:4-7; 10:51-52; 12:46-49; 13:15-17, emphasis added; Figures 1-2, 4-6.

101. As such, Petitioner submits that “recovering the manganese dioxide precipitate” should be construed as recovering the manganese dioxide precipitate by filtration, centrifugation, electrochemically or known like processes.

h. “providing iron (III)”

102. Claim 13 of the ‘117 patent refers to “providing iron (III)”. The Specification explains that:

Typically, brine will have an iron (II) salt present naturally. In other embodiments, an iron (II) salt or **iron (III) hydroxide can be added** to the brine to achieve a certain concentration of iron (II) salt or iron (III) hydroxide relative to the silica or silicon containing compounds present in the brine.

...

In another embodiment, iron (III) hydroxide can be produced by adding a solution of iron (III) chloride to the brine, which on contact with the more neutral brine solution, will precipitate as iron (III) hydroxide.

EX 1001, 6:27-7:2, emphasis added.

103. The ‘117 patent describes “iron (III)” as “iron (III) hydroxide” or as “a solution of iron (III) chloride”. Iron (III) hydroxide is better understood as an intermediate that is formed by the combination of water with oxidized ferrous (iron (II)) ions to produce ferric oxyhydroxide.

104. For purposes of this Petition, Petitioner proposes that the term “iron (III)” be interpreted as iron (III) hydroxide, iron (III) oxyhydroxide, iron (III) chloride, or ferric ions.

VII. DISCUSSION OF THE PRIOR ART

a. Maimoni, A., A Cementation Process for Minerals Recovery from Salton Sea Geothermal Brines, Lawrence Livermore Laboratory, January 26, 1982.

105. I have reviewed *Maimoni* in connection with the instant IPR.

106. *Maimoni* was not of record, nor was it considered, during the prosecution of the ‘117 patent.

107. *Maimoni* was written pursuant to a U.S. government sponsored research agreement and was made available to the public by the Lawrence Livermore Laboratory as a printed publication. *Maimoni* has a manuscript date of January 26, 1982. EX 1004, at 1. *Maimoni* is a prior art reference under 35 U.S.C. § 102(b).

108. *Maimoni* is from the same field of endeavor as that of the ‘117 patent, *i.e.*, recovery of minerals and metals from geothermal brines, including, specifically, geothermal brines from the Salton Sea. EX 1004, at Abstract. In my opinion, a POSITA who sought to solve the problem set out in the ‘117 patent would find *Maimoni* to be of particular relevance.

109. The ‘117 patent indicates that brines from the Salton Sea would be appropriate for use with the method claimed therein. “This invention relates to a method for the selective recovery of manganese and zinc from geothermal brines ...”, (EX 1001, at Abstract) and, “[b]rines can be obtained from natural sources, such as, Chilean brines or Salton Sea brines, geothermal brines, sea water, ...”. *Id.*, 6:42-43, emphasis added. *Accord*:

Geothermal brines, such as those found in the Salton Sea, can include many dissolved metal salts, including alkaline, alkaline earth, and transition metal salts. In one embodiment, **the present invention**

provides a method for separating manganese, as well as zinc, lead, and silver, from brines, particularly geothermal brines.

Id., 6:48-54.

110. In my opinion, a POSITA who was seeking to solve the problem set out in the ‘117 patent would find the *Maimoni* reference to be especially relevant.

111. *Maimoni* reports a brine treatment process that begins with a geothermal brine from the Salton Sea (Magmamax No. 1), selectively removes silica and iron from the brine before removing and extracting various minerals and metals, including manganese, zinc and lithium from it. EX 1004, 11-12.

112. *Maimoni* discusses that the substantial amount of iron silicate scale deposited by Salton Sea brines during equipment operation has been a major impediment on the development of geothermal energy in the area, and that silica and iron scale control and removal is a key part of any process for handling Salton Sea geothermal brines. *Id.*, at 10, 22. Moreover, *Maimoni* teaches “[b]rine reinjection would be considered a basic necessity for long-term operations”. *Id.*, at 8; *see also* Figs. 5 and 7.

113. *Maimoni* discusses that mineral recovery from Salton Sea brines has been widely acknowledged, and reviewed the prior work of Hazen’s laboratory and pilot plant tests in the Salton Sea. *Id.*, at 13-17.

114. *Maimoni* reports that Hazen separated iron from manganese and zinc by selective precipitation of the respective hydrated oxides, and that Hazen’s process

was based on selective precipitation of the hydroxides using lime and oxidizing ferrous to ferric iron by sparging air through the brine. *Id.*, at 14.

115. *Maimoni* further reports that Hazen's process also recovered 90% of the lithium from the brine. *Id.*, at 14-17.

116. *Maimoni* further reports Hazen recognized that it would be advantageous to remove the silica and iron present in the brine before precipitating the heavy metal hydroxides (*e.g.*, zinc and manganese), (*Id.*, at 14) and further recognized:

Silica control and removal is a key part of any process for handling Salton Sea brines. In this context, LLNL experimental work on brine acidification, the effects of organic additives, and **methods for precipitating, thickening, and filtering the silica needs to be considered in any future design studies.**

Id., at 22, emphasis added.

117. Table 5 and Figure 5 in *Maimoni* show the complete design flow sheet and compositions of Hazen's 15-gpm pilot plant, which are reproduced below. *Id.*, at 15-17.

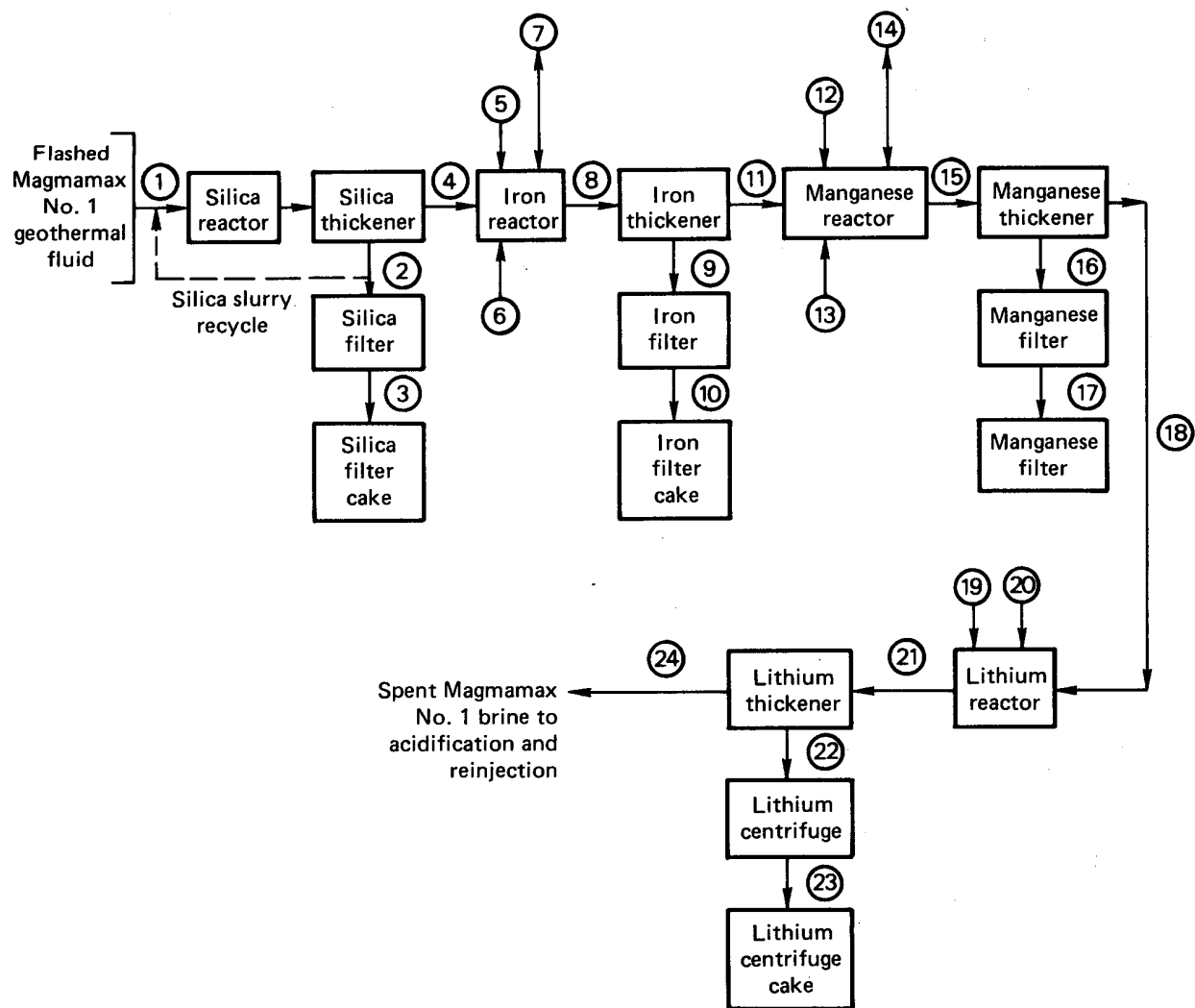


Figure 5. Process materials balance of Magmamax No. 1 brine (Hazen Research).

Table 5. Process flow sheet for Magmax No. 1 brine (Hazen Research, Inc.).

	Stream No.											
	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	230 ppm total 187 ppm solid	1.6 lb/h 10.2 wt%	1.6 lb/h 60 wt%	43 ppm				43 ppm	0.16 lb/h solids		22 ppm	
Fe	255 ppm			255 ppm				255 ppm total	375 lb/h solids		26 ppm	
Zn	333 ppm			333 ppm				333 ppm			333 ppm	
Mn	775 ppm			775 ppm				775 ppm			775 ppm	
Pb	70 ppm			70 ppm				70 ppm	0.13 lb/h solids		56 ppm	
Li	182 ppm			182 ppm				182 ppm			182 ppm	
Inertia	22.1%			22.1%				22.1%			22.1%	
H ₂ O	77.7%			77.7%			7 lb/h	77.7%			77.1%	
Specific grey	1.135	1.20		1.135	1.22			1.14	1.32	1.9	1.13	1.22
Temp. °C	93	93	93	93	25	29	92	92	92	92	92	25
Temp. °F	200	200	200	200	77	85	198	198	198	198	198	77
Flow, gpm	15	0.025		15	0.025			15	0.03		15	0.088
Flow, gph	900	1.5		900	1.50			901	1.8		901	5.25
Flow, cfm	—	—				5.0	6.2					
Flow, lb/h	8523	15.0	2.67	8520	15.3			8528	20	6.8	8508	54
Specific heat Btu/lb °F	0.85	0.78	0.46	0.85	0.77			0.85		0.48	0.85	0.77
Heat Btu/h	1.45 × 10 ⁶	2340	2.46	1.45 × 10 ⁶	2471			144 × 10 ⁶		646	144 × 10 ⁶	10,656
Density	9.47 lb/gal	9.99 lb/gal	≈50 lb/ft ³	9.47 lb/gal	10.2 lb/gal			951 lb/gal	11.0 lb/gal	15.8 lb/gal	944 lb/gal	10.2 lb/gal
NH ₃	352 ppm			352 ppm				352 ppm			352 ppm	
	Post-flash Magmax No. 1 brine input	SiO ₂ thickener underflow at 11 wt% solids	SiO ₂ filter cake	Brine feed to iron reactor	40% w/v Ca(OH) ₂ slurry	Air sparge to iron reactor	Vent gases from iron reactor	Iron slurry to thickener	Iron thickener underflow at 20 wt% solids	Iron filter cake	Iron thickener overflow	40% w/v Ca(OH) ₂ slurry

Table 5. (Continued.)

	Stream No.											
	13	14	15	16	17	18	19	20	21	22	23	24
SiO ₂												
Fe			26 ppm	0.21 lb/h		13 ppm			13 ppm			13 ppm
Zn			333 ppm	4.11 lb/h		17 ppm			17 ppm			17 ppm
Mn			775 ppm	10.06 lb/h		39 ppm			39 ppm			39 ppm
Pb			56 ppm	0.48 lb/h		6 ppm			6 ppm			6 ppm
Li			182 ppm			182 ppm			182 ppm	43 lb/h solids		18 ppm
Inertia			22.1%			22.1%			22.1%			22.1%
H ₂ O		20 lb/h	777%			77.8%			77.0%			77.0%
Specific grey			1.132	1.303	1.86	1.13	1.109	1.315	1.13	1.434	1.86	1.13
Temp. °C	29	90	90	90	90	90	25	25	90	90	90	90
Temp. °F	85	195	195	195	195	195	77	77	195	195	195	195
Flow, gpm			15	0.11		15	0.22	0.05	15.3	0.15	0.1	15
Flow, gph			904	6.8	1.6	902	13.6	2.8	918	9.2	5.8	912
Flow, cfm	12.4	16.0										
Flow, lb/h			8540	74	24.8	8515	126	31	8672	110	78	8594
Specific heat Btu/lb °F			0.85			0.85	0.78	0.67	0.85		0.48	0.85
Heat Btu/h			1.41 × 10 ⁶		2176	1.41 × 10 ⁶	7568	16,000	1.44 × 10 ⁶		7301	1.43 × 10 ⁶
Density			9.45 lb/gal	10.9 lb/gal	15.5 lb/gal	9.44 lb/gal	9.24 lb/gal	10.9 lb/gal	9.45 lb/gal	12.0 lb/gal	15.5 lb/gal	9.43 lb/gal
NH ₃		3.0 lb/h	352 ppm			35 ppm			35 ppm			35 ppm
	Air sparge to manganese reactor	Vent gases from manganese reactor incl. ammonia	Manganese slurry to thickener	Manganese thickener underflow at 20 wt% solids	Manganese filter cake	Manganese thickener overflow	NaAlO ₂ solution 30 wt% NaAlO ₂	AlCl ₃ solution 40 wt% AlCl ₃	Lithium aluminate slurry to thickener	Lithium aluminate thickener underflow at 20 wt% solids	Lithium aluminate centrifuge cake	Lithium aluminate thickener overflow

118. Based on my review of *Maimoni*, I have prepared the following explanation of the Hazen process summarized in *Maimoni*. The process steps in Figure 5 are in accord with the Streams in Table 5. An explanation of each stream in Table 5 has been provided in the text that follows.

119. Stream 1. Flashed Magmamax No. 1 geothermal brine is fed into a silica reactor. The Magmamax No. 1 brine was obtained from the Salton Sea Geothermal Field (Figures 1 and 2) and generally has the elemental constituents reported in Table 2.

120. As the Magmamax No. 1 geothermal brine is produced from the wellhead, silica in the brine has already begun to precipitate as part of the flashing process. It should be noted that flashing might be expected to increase concentrations of all components due to removal of a portion of the brine water in the form of steam. The total silica concentration in Table 5 is reported to be 230 ppm with 187 ppm being present as solid. The inlet flow to the pilot plant then proceeds to a silica reactor designed to precipitate silica on silica slurry recycle. This slurry recycle is also known as “seed” and the “seeding” limits silica scaling on piping. The slurry from the silica reactor proceeds to the silica thickener (also known as a clarifier). In the silica thickener, silica binds to the seeding material and precipitates to the silica thickener underflow of Stream 2.

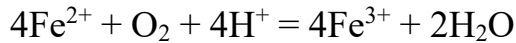
121. Stream 2. A slipstream from the underflow of the silica thickener is recycled back to Stream 1 to provide “seed” to the silica reactor. The bulk of the precipitated, thickened slurry from the underflow of the silica thickener is filtered on a filter press forming a silica filter cake (Stream 3). The silica thickener overflow (Stream 4) is a clarified brine having a silica concentration reduced from 230 ppm to 43 ppm.

122. Stream 3. The silica filter cake contains 60 wt% filtered solids (primarily silica) and 40 wt% moisture.

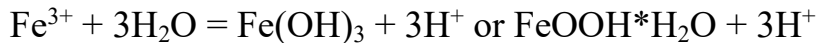
123. Stream 4. This stream is the clarified brine overflow from the silica thickener. Since much of the silica has been precipitated in the silica reactor and the silica thickener, the clarified overflow brine now contains only 43 ppm silica in solution. This clarified brine is fed to the iron reactor of Stream 4.

124. Stream Nos. 5, 6 and 7. The clarified brine of Stream 4 that is fed into the iron reactor initially contains 255 ppm iron and 43 ppm silica. A 40% slaked lime slurry ($\text{Ca}(\text{OH})_2$) is added (Stream 5) and air is injected or sparged into the iron reactor (Stream 6) to precipitate ferrous iron originally present in the brine as ferric hydroxide ($\text{Fe}(\text{OH})_3$) and/or ferric oxyhydroxide (FeOOH). The additional silica coprecipitates with the iron, especially ferric iron generated by the sparged Salton Sea geothermal brine in the iron reactor.

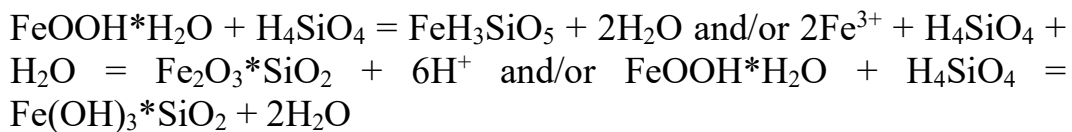
125. When air is injected into the iron reactor, ferrous ions in the brine are converted into ferric ions:



The Fe^{3+} reacts with water to form ferric hydroxide, $\text{Fe}(\text{OH})_3$, or ferric oxyhydroxide hydrate, $\text{FeOOH} \cdot \text{H}_2\text{O}$:



Once ferric oxyhydroxide hydrate is generated, it will react quantitatively with silica (as silicic acid) to form insoluble ferric silicate precipitate:



Ferric ion, ferric hydroxide and ferric oxyhydroxide hydrate are excellent precipitating agents for silica, and it is well-known that silica in water or brine can be precipitated (removed as a solid) with ferric ion, ferric hydroxide or ferric oxyhydroxide hydrate.

126. Therefore, when *Maimoni* aerates Salton Sea geothermal brine, he precipitates ferric silica solid and there is sufficient iron content in the brine to react with the silica to drive the silica concentration down from 43 ppm to 22 ppm and the iron concentration down from 225 ppm to 26 ppm (Stream 11). By maintaining the pH of the brine with lime, the silica and iron precipitate quantitatively to yield a clarified brine having low iron and silica concentrations.

127. Air and any displaced gases are vented from the iron reactor (Stream 7).

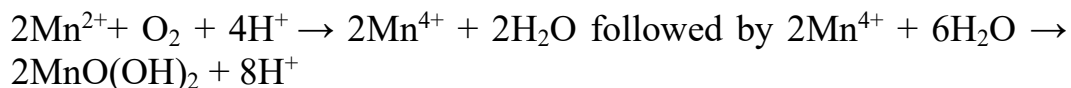
128. Stream 8. The mixture of clarified brine and precipitated iron leave the iron reactor and pass to the iron thickener, which again is a clarifier. The clarified brine overflow is fed into the manganese reactor (Stream 11). Meanwhile, the precipitated solids containing silica bound to the ferric iron settle to the underflow of the iron thickener. The solids concentration is 20 wt% most of which is iron, but some is silica and lead (Stream 9).

129. Stream Nos. 9 and 10. Like the silica removal process, the iron silicate-laden solids from the iron thickener underflow are filtered and the filter cake is generated.

130. Stream 11. This is the iron thickener/clarifier overflow brine. The concentration of iron in the iron reactor and thickener has decreased from 255 to 26 ppm. Silica has been coprecipitated by the ferric iron to decrease its concentration from 43 to 22 ppm. Some lead has been precipitated with the ferric silicate to decrease its concentration from 70 ppm to 56 ppm. Also, the concentration of zinc and manganese has held constant at 333 ppm and 775 ppm, respectively, through the silica and iron reactors and thickeners.

131. Stream 12, 13 and 14. The iron thickener/clarifier overflow brine enters the manganese reactor (Stream 11). In the manganese reactor like in the iron reactor, a 40% slacked lime/calcium hydroxide slurry is added (Stream 12) and air is again injected into the manganese reactor (Stream 13) to precipitate manganese as $MnO(OH)_2$. The unreacted air and sparged gases are vented from the reactor (Stream

14). One of the sparged gases is ammonia, signifying that the pH of the brine is greater than about 9. Manganese in brine is initially present as Mn^{2+} , and the reaction of Mn^{2+} with air oxidizes the manganese from a 2+ state to a 4+ state:



Since there is a net gain of hydrogen ions, the pH would drop except for the addition of slacked lime/calcium hydroxide slurry to maintain the pH level.

132. Stream 15. The mixture of brine and precipitated manganese hydroxide leave the manganese reactor and pass to the manganese thickener, which again is a clarifier. The clarified manganese thickener overflow is fed to the lithium reactor (Stream 18). Meanwhile, the precipitated manganese solids (containing iron, zinc, and lead) settles to the underflow of the manganese thickener (Stream 16). The solids concentration is 20 wt% most of which is manganese oxyhydroxide, $MnO(OH)_2$.

133. Stream 16 and 17. These steps are similar to those in the silica and iron reaction processes steps of Stream Nos. 2-3 and 9-10, the manganese-laden solids from the manganese thickener underflow are filtered, and the manganese-rich filter cake is generated. On page 9, *Maimoni* reports that the filter cake contained 47.3% Mn, 18.2% Zn, 2.6% Pb and 0.6% Fe. The forms of lead and zinc in the precipitate are $Pb(OH)_2$, possibly PbO_2 and $Zn(OH)_2$. Aeration does not oxidize zinc.

134. Stream 18. This is the manganese thickener/clarifier overflow brine. The concentration of manganese at the manganese reactor and the manganese thickener

has decreased from 755 to 39 ppm. Some lead has been precipitated with the manganese to decrease its concentration from 56 to 6 ppm. Most of the zinc has also precipitated and its concentration has decreased from 333 to 17 ppm.

135. As noted above, silica coprecipitates with the iron based on the disclosed processing conditions of *Maimoni*. While the concentration of silica is not reported after Stream 11, the concentration of silica in the brine decreases necessarily quantitatively along with the reported decrease in iron between Streams 15 and 18. That is, as can be seen in Table 5, iron precipitated with additional processing between Streams 15 and 18 and its concentration decreased in half from 26 ppm in Stream No. 15 to 13 ppm in Stream No. 18. As such, while not explicitly reported in the table, the silica concentration necessarily also decreased quantitatively along with the reported decrease in iron. Thus, the reported silica concentration of 22 ppm in Stream 11 was reduced to about 10 ppm or less in Stream No. 18 and, in view of the processes reported, the silica concentration remained about 10 ppm or less in the remaining streams of Table 5.

136. Table 5 discloses a recoverable amount of lithium in Stream 18 of 182 ppm. At this point in the process and before entering the lithium reactor, the brine stream has been polished and clarified to precipitate and remove substantially all the silica, iron, manganese, and zinc to ensure a clean lithium product is produced.

137. Stream 19 and 20. The manganese thickener overflow brine moves into the lithium reactor (Stream 18). In the lithium reactor, sodium aluminate (NaAlO_2) and aluminum chloride (AlCl_3) are injected into brine at concentrations of 30 and 40 wt%, respectively. This reaction is designed to precipitate lithium aluminate (LiAlO_2).

138. Stream 21. This mixture is lithium aluminate slurry and brine is sent from the lithium reactor to the lithium thickener/clarifier.

139. Stream 22 and 23. The lithium thickener underflow slurry is sent to a centrifuge (Stream 22), where a lithium-rich centrifuge cake is prepared (Stream 23). The underflow slurry contains 39 wt% lithium aluminate.

140. Stream 24. This is the lithium thickener/clarifier overflow brine that has been processed to precipitate and remove silica, iron, manganese, zinc and lithium. The concentration of lithium in the lithium reactor has been reduced from 182 to 18 ppm in the lithium thickener. In the lithium precipitation step, no more iron, zinc, manganese or lead have been precipitated, and therefore, no contaminants of the lithium aluminate according to *Maimoni*. This metal-depleted brine is pH-adjusted with acid and the spent Magmamax No. 1 brine is reinjected back into the geothermal reservoir.

141. Based on the foregoing results of Hazen's pilot plant, *Maimoni* proposed a sequential cementation process based on a modified Hazen process that would result

in silica, iron hydroxides, manganese, and zinc hydroxides to be uncontaminated by other heavy metal elements. *Id.*, at 18 and Figure 7.

142. Figure 7 of *Maimoni* is reproduced below:

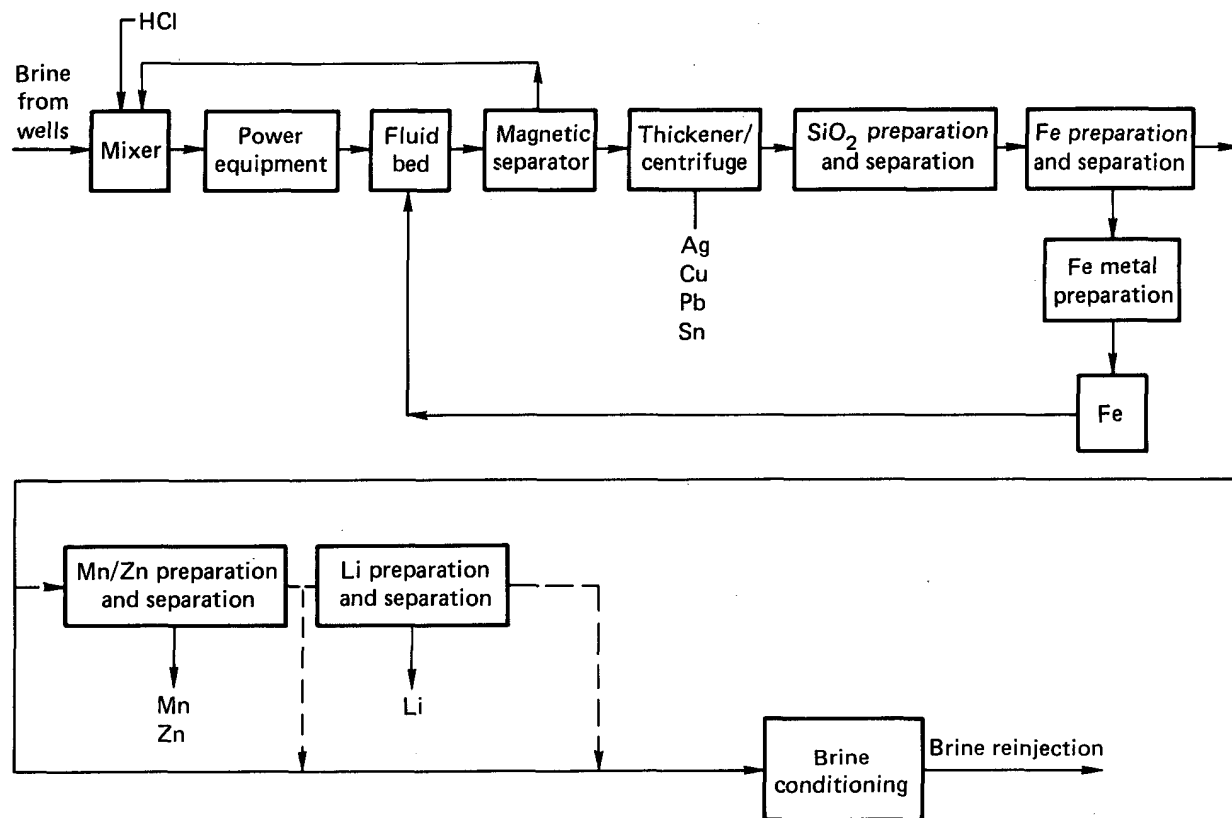


Figure 7. Steps in minerals recovery from Salton Sea brines.

143. As can be seen from Figure 7, *Maimoni* discloses a process for mineral recovery from Salton Sea brines that includes sequentially separating silica (SiO₂), iron, manganese and zinc from the brine, then separating lithium from the clarified brine, and lastly reinjecting the brine back into the reservoir. *Id.*, at 21.

144. *Maimoni* states that his proposed process would be advantageous because the resulting silica, iron hydroxides, manganese, and zinc hydroxides would be uncontaminated by the other heavy elements. *Id.*, at 23.

145. *Maimoni* further states that:

A 1000-MWe power plant could recover 14-31% of the U.S. demand for manganese together with significant quantities of zinc and lead. The potential for lithium recovery is very large; one such 1000-MWe plant could recover between 31 and 65 thousand metric tons of lithium per year (metal equivalent), compared to the 1980 total world sales of about 7.2 thousand metric tons.

Id., at 4.

146. *Maimoni* further states that his process would be advantageous because the manganese and zinc mixed hydroxide product would be “quite pure”. *Id.*, at 21.

b. Bourcier, et al., *Recovery of Minerals and Metals from Geothermal Fluids*, 2003 SME Meeting, Feb. 24 – Feb. 26, 2003.

147. I have reviewed *Bourcier* in connection with the instant IPR.

148. *Bourcier* was not of record, nor was it considered, during the prosecution of the ‘117 patent.

149. *Bourcier* was published September 8, 2005, by the Lawrence Livermore National Laboratory. This publication summarizes work that was previously presented at a 2003 SME Annual Meeting in Cincinnati, OH, which meeting took place February 24-26, 2003. EX 1005, at 1. *Bourcier* is prior art under 35 U.S.C. § 102(b).

150. *Bourcier* is from the same field of endeavor as that of the ‘117 patent, *i.e.*, it deals with extracting valuable minerals and metals from geothermal brines. *Bourcier* summarizes mineral and metal extraction projects from various geothermal brine sources, including a Salton Sea geothermal brine, which is one example of a geothermal brine that could be a source for minerals and metals according to the methods of the ‘117 patent. EX 1005, at 12. Salton Sea geothermal brines are specifically acknowledged in the ‘117 patent as being appropriate for use with its invention. EX 1001, 6:5-8.

151. *Bourcier* notes that potential mineral and metal products from these geothermal brines include silica, zinc, lithium, and other materials. “Recovery of minerals and metals from geothermal fluids can be viewed as ‘solution mining by nature’, followed by application of established or new hydrometallurgical techniques for isolation and purification.” EX 1005, at 5.

152. *Bourcier* further teaches that the Salton Sea is one of the most metal-rich geothermal fluids in the world, and is especially enriched in metals that form strong hydrothermal complexes with chloride, such as zinc, copper, lead and silver. *Id.*, at 11.

153. In my opinion, a POSITA who sought to solve the problem set out in the ‘117 patent would find *Bourcier* to be of particular relevance.

154. *Bourcier* teaches that lithium is often enriched in geothermal brines, and that “[l]ithium can be extracted from geothermal fluids by direct precipitation as lithium salts, or captured using ion exchange resins.” *Id.*, at 8.

155. *Bourcier* also recognizes that:

Geothermal fluids contain significant concentrations of potentially valuable mineral resources. Although their mineral content was often considered more a nuisance than an asset, there is now increasing interest in improving the economics of geothermal energy by co-producing and marketing some of the dissolved constituents. Simple cost-effective methods are needed to extract mineral byproducts from geothermal fluids. Useful methods may have already been developed in the hydrometallurgical industry that could be modified for use with geothermal fluids. Although the enrichment of target elements in geothermal fluids is not as high as the enrichment in fluids commonly treated with hydrometallurgical methods, the costs associated with resource extraction from geothermal fluids are potentially low for several reasons.

Id., at 5.

156. *Bourcier* discusses that metals and salts can be recovered from geothermal fluids using sorption, evaporation and precipitation. *Id.*, at 7-8.

157. *Bourcier* recognizes that silica is a “ubiquitous component of geothermal fluids and must be removed or reduced in concentration to allow for other components to be removed.” *Id.*, at 8. *Bourcier* goes on to discuss that many different methods have been used to precipitate silica from geothermal brines, such as pH modification, temperature modification and seeding.

158. In discussing a case history involving a Salton Sea brine, which is “[o]ne of the most metal-rich geothermal fluids in the world”, the zinc and silica extraction work at CalEnergy’s Salton Sea facility is detailed. *Id.*, at 11-13.

159. Speaking specifically of the CalEnergy project which used Salton Sea brine: “Silica must be removed from the fluid for the zinc extraction processed to be successful, if not, the ion exchange resins are quickly covered by silica precipitates and fail to efficiently extract zinc.” *Id.*, at 12, emphasis added.

160. *Bourcier* discloses:

In geothermal systems that have been acidified to control silica scale formation, adding base to increase the pH will induce silica precipitation. ... By adding base, the rate of silica polymerization increases and leads to the formation of silica colloids, which then flocculate to form silica precipitates. Cooling can also be used to precipitate silica. A rapid drop in temperature increases the degree of silica supersaturation and leads to nucleation of silica colloids. Finally, seed silica can be added to geothermal fluids to act as nucleation sites for silica precipitation...

Id., at 8.

161. Silica is removed as follows:

The silica is currently removed upstream using a clarification process that combines lime addition and silica seeding. The pH increase accompanying lime addition accelerates silica polymerization, and silica seeds enhance precipitation. The silica is removed by flocculant-aided settling.

Id., at 11.

162. A POSITA would appreciate and *Bourcier* recognizes that the silica removal process will also precipitate iron along with the silica in the process discussed above. “Geothermal silicas that do not meet the compositional requirements for the intended market can be acid leached to remove unwanted contaminants such as iron and zinc.” *Id.*, at 7. “The silica precipitated with this method has significant amounts of contaminants such as iron ...”. *Id.*, at 12.

163. *Bourcier* reports that CalEnergy removed zinc from the Salton Sea geothermal brine by passing it over an anionic ion exchange (IX) bed, which removes the zinc primarily as ZnCl_4^{2-} . The IX resin was then eluted with an acidic solution that contains a reducing agent, and iron, arsenic and lead were also extracted with zinc in the IX process. The zinc was then removed from the elute in a solvent extraction process (SX) that utilized a water immiscible cationic extractant. The zinc-loaded SX extractant was then further processed to produce metallic zinc. *Id.*, at 11-12.

164. *Bourcier* reports that CalEnergy also had “investigated methods for extracting manganese from their brines” *Id.*, at 13. CalEnergy utilized diethylhexyl phosphoric acid and a quaternary amine in a solvent extraction process to extract manganese from the brine, and the extracted manganese can be further processed to produce electrolytic manganese dioxide for use in batteries. *Id.*, at 13.

c. Christopher, et al., *The Recovery and Separation of Mineral Values from Geothermal Brines*, (contract HO144104, Hazen Research Inc.), Bureau of Mines OFR 81-75, June 12, 1975.

165. I have reviewed the *Christopher* reference in connection with the instant *inter partes* review.

166. *Christopher* was not of record, nor was it considered, during the prosecution of the ‘117 patent.

167. *Christopher* was written pursuant to a U.S. Government sponsored research agreement and was published by United States Department of the Interior, Bureau of Mines. *Christopher* has a report date of June 12, 1975, and a University of Utah Libraries stamp dated June 29, 2005. EX 1006, at 1-2. *Christopher* is a prior art reference under 35 U.S.C. § 102(b).

168. *Christopher* is from the same field of endeavor as that of the ‘117 patent, *i.e.*, recovery and separation of minerals from geothermal brines, namely, Sinclair No. 4 geothermal brines from the Salton Sea. *Id.*, at 6.

169. In my opinion, a POSITA who sought to solve the problem set out in the ‘117 patent would find *Christopher* to be of particular relevance.

170. *Christopher* summarizes the work done and results obtained by Hazen between July 1974 and February 1975 to determine methods for recovery of mineral values from geothermal brines. *Id.*, at 7.

171. *Christopher* discloses “[w]ellhead brine, both pre-flash and post-flash, from the Sinclair No. 4 well, Imperial Valley, California was chosen for the study.” *Id.* “The subject laboratory process study on recovery and separation of minerals from Sinclair No. 4 geothermal brines developed methods for recovering iron and manganese hydrated oxide compounds as separate components essentially quantitatively. In addition, lead and zinc values were also removed, essentially quantitatively, as co-precipitated compounds together with the hydrated manganese oxides.” *Id.*, at 6.

172. *Christopher* discusses processes that have been developed for the recovery of iron, manganese, zinc, lithium, and other minerals and metals from the geothermal brine. *Christopher* notes that:

Greater than 99% of the total heavy metal values were separated at under nonoxidizing conditions using lime as a precipitant. As an alternative, iron may be selectively precipitated as a hydrated magnetic oxide at pH = 6.0, again using lime as precipitant, but under controlled air oxidation. The remaining heavy metals were subsequently brought down with lime under oxidizing alkaline conditions. Iron was recovered as a magnetic oxide product containing 68% Fe, manganese, zinc, and lead as a mixed oxide product containing 47.3% Mn, 18.2% Zn, and 2.8% Pb. Lithium was separated by precipitation with aluminum hydroxide at pH = 7.5. Recoveries of greater than 99% were obtained.”

Id., at 7, emphasis added.

173. *Christopher* discloses flashing a fresh wellhead geothermal brine in order to provide the Sinclair No. 4 “post-flashed” brine. When flashing the fresh wellhead brine, the temperature of the supersaturated Salton Sea geothermal brine decreases

and the silica and other metals in the brine precipitate. In *Christopher*, flashing the fresh wellhead brine caused the silica in the brine to precipitate and the dissolved silica concentration was reduced from about 750 ppm in the pre-flash, wellhead brine to about 40 ppm in the post-flash, treated geothermal brine. *Id.*, at 8-9.

174. Table 1 shows the silica (reported as Si) concentration of 40 ppm in the post-flash brine:

Table 1
Typical Composition of Sinclair No. 4 Brine

Element	ppm	Element	ppm	Element	ppm	Element	ppm
Ag	0.5	Ce	10	Mn	2000	Se	2.5
Al	0.6	Cu	0.5	Mo	10	<u>Si</u>	<u>40</u>
As	3.	F	10	Na	70,000	SO ₄	0.04
B	400	<u>Fe</u>	<u>1200</u>	Nb	0.1	Sr	600
Ba	200	Ga	0.5	NH ₄	650	Ta	6
Br	200	Ge	1.	Ni	0.5	Tl	2.5
Ca	35,000	I	0.5	P	0.5	V	0.3
Cd	0.9	K	19,000	Pb	100	<u>Zn</u>	<u>500</u>
Cl	190,000	<u>Li</u>	<u>250</u>	Rb	25	Zr	8
Cr	2	Mg	150	S	0.1		

Id., at 8, highlighting added.

175. After discussing the composition of typical, post-flashed geothermal brines, *Christopher* turns to a discussion of the removal of the major heavy metals (*e.g.*, manganese, iron, zinc and lead) by precipitation using a lime slurry to control the pH under varying oxidation conditions for ferrous-ferric ions, *i.e.*, maintained in a reduced state under nitrogen, under normal atmospheric conditions, and under air

sparge to maximize air oxidation. *Id.*, at 10-11. As shown in Figure 2 of *Christopher*, the immediate and complete precipitation of manganese, iron, zinc and lead can be achieved.

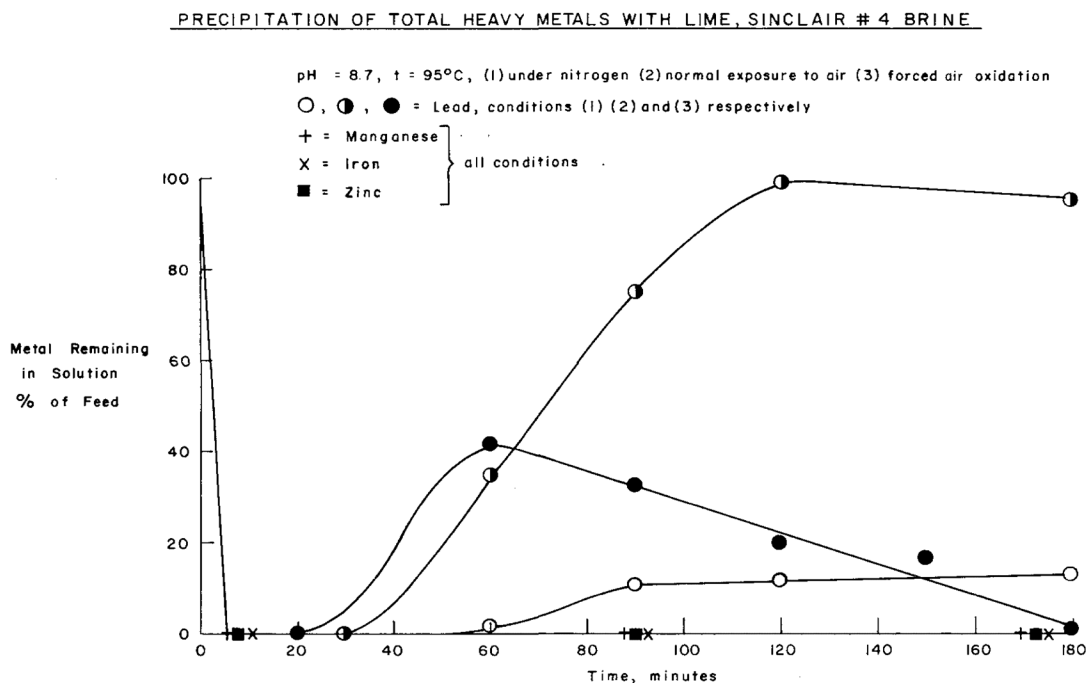


FIGURE 2
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Id., at 14. As can be seen, the concentrations of zinc (black squares) and iron (“X”) are reduced to nearly zero (less than 5 mg/kg) within the first few minutes of treatment.

176. On the basis of the above work, *Christopher* evaluated a 20-minute contact time under nonoxidizing conditions of the lime precipitation process. “Analytical data on the feed and product brines and the dried solid product are given in Table 3. Note that magnesium and sulfate, in addition to manganese, iron, zinc, and lead, are effectively removed from the brine.” *Id.*, at 12.

177. Table 3 shows a zinc concentration of 0.004 g/L (3.4 mg/kg²), no reported silica (either as elemental Si or as silicon dioxide (SiO₂)), an iron concentration of 0.0053 g/L (4.5 mg/kg), and a recoverable lithium concentration of 0.261 g/L (221 mg/kg) in the treated geothermal Product Brine:

Table 3
Purification of Brine by Precipitation
of Heavy Metal Hydroxides

Element	Concentration		Washed and Dried Product Solid Wt., %
	Feed Brine g/l	Product Brine g/l	
Ba	0.223	0.207	0.002
Ca	34.6	36.6	12.4
Pb	0.139	<0.001	1.52
<u>Li</u>	<u>0.255</u>	<u>0.261</u>	0.06
Mg	0.150	0.0014	2.09
Mn	1.63	0.002	17.3
<u>Fe</u>	<u>0.88</u>	<u>0.0053</u>	11.0
Na	69	86	0.0088
Sr	0.710	0.719	0.009
K	19.1	18.7	0.007
<u>Zn</u>	<u>0.497</u>	<u>0.004</u>	6.03
SO ₄	0.042	<0.001	-
NH ₄	0.797	0.007	-

Id., at 12, highlighting added.

178. *Christopher* goes on to selectively precipitate and separate iron from the post-flash brine by precipitation of ferrous hydroxide or from the oxidizing lime (Figure

² mg/kg=(g/L*1000)/1.18kg/L due to the density of Salton Sea geothermal brines.

4) or ammonia (Figure 5) slurry to control pH in order to remove 99% of iron to produce an “iron free brine”. *Id.*, at 16-22, 42.

179. Christopher states: “Subsequent precipitation of manganese, lead, and zinc would thus provide a solid product much lower in iron and of greater commercial value than that produced by the process given in the preceding section.” *Id.*, at 16.

180. *Christopher* conducted four tests “in which brine, adjusted to pH 5.5, 6.0, 6.5, and 7.0 at 95°C, was continuously sparged with air at approximately 0.5 liters per minute for three hours.” *Id.*

181. “At pH = 6, 97% of the iron has been removed from solution with essentially no loss of manganese, zinc, and lead.” *Id.*; see also Figure 6, reproduced below.

MAGNETIC IRON OXIDE FORMATION: DISTRIBUTION OF HEAVY METALS

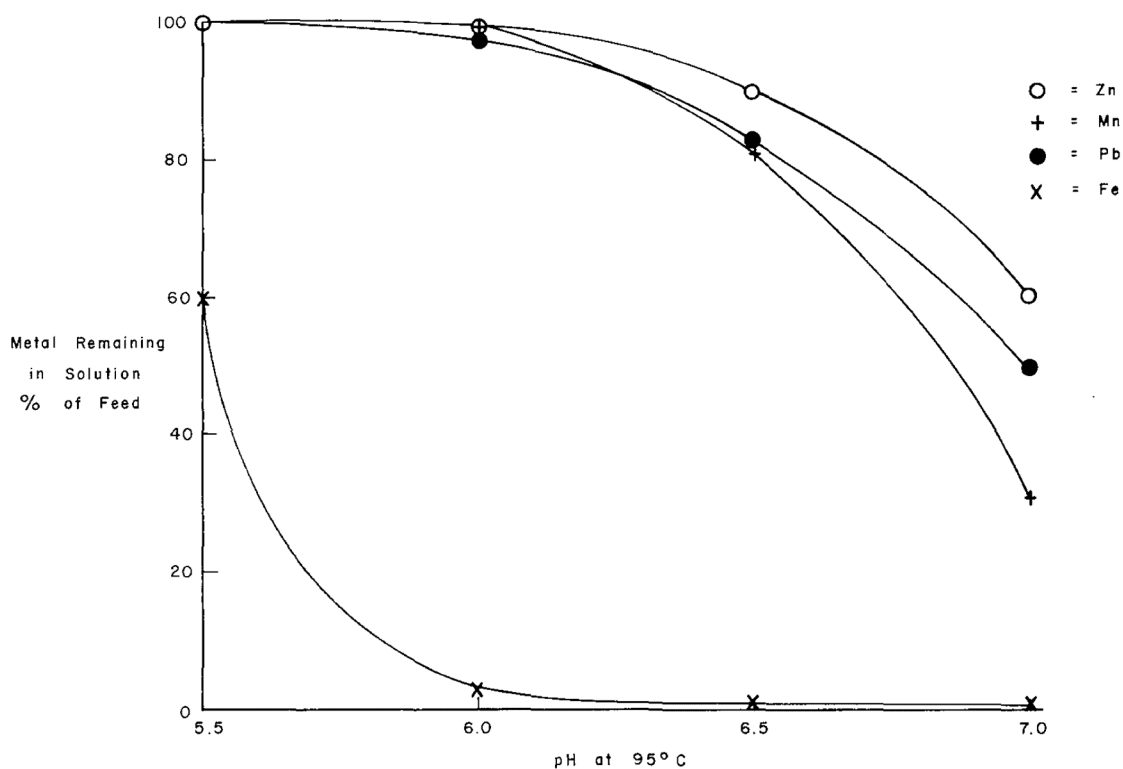
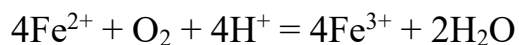


FIGURE 6
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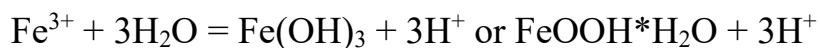
Id., at 20.

182. The silica in the pre-flash and post-flash brines of *Christopher* coprecipitates with iron based on at the disclosed pH and oxidizing conditions, thereby further reducing the concentration of silica.

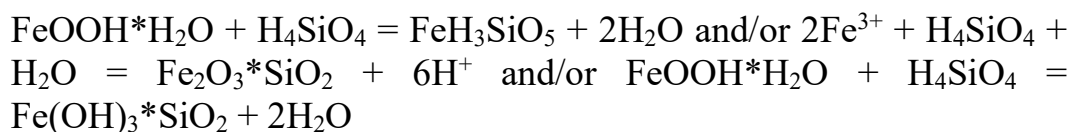
183. When air is injected into the iron reactor, ferrous ions in the brine are converted into ferric ions:



The Fe^{3+} reacts with water to form ferric hydroxide, $\text{Fe}(\text{OH})_3$, or ferric oxyhydroxide hydrate, $\text{FeOOH}\cdot\text{H}_2\text{O}$:



Once ferric oxyhydroxide hydrate is generated, it will react quantitatively with silica (as silicic acid) to form insoluble ferric silicate precipitate:



Ferric ion, ferric hydroxide and ferric oxyhydroxide hydrate are excellent precipitating agents for silica, and it is well-known that silica in water or brine will be precipitated (removed as a solid) with ferric ion, ferric hydroxide or ferric oxyhydroxide hydrate.

184. In connection with Table 3 and Figure 6 above, (*Id.*, at 12, 20), by oxidizing ferrous to ferric iron (or seeding with ferric iron) and maintaining the pH of the brine in the 4.5 to 6.5 range with lime (or caustic soda or ammonia), the iron precipitates quantitatively with silica and a POSITA could easily tune the parameters of the process to yield a silica and iron free brine.

185. Therefore, when *Christopher* aerates Salton Sea geothermal brine, he precipitates ferric silica solid and there is a sufficient concentration of iron in the brine to react with the silica to reduce the silica concentration in the pre-flash or post-flash brine down to about 5 mg/kg or less in the Product Brine of Table 3 and

to about 1 ppm or less in Manganese Precipitation Discharge Liquor (3) of Figure 20.

186. *Christopher* then goes on to disclose that the heavy metals (*e.g.*, manganese, zinc, and lead) are precipitated from the iron free brine before recovery of lithium.

Iron free brine was prepared by precipitation and separation of magnetic iron oxide in accordance with the previous section. The liquor was agitated for three hours, with sufficient lime slurry added to establish and maintain a pH of 8. 7. Analysis for manganese, zinc, lead, and iron was performed at intervals. Two tests were run: (1) under nitrogen to preclude oxidation of manganous ion, and (2) under a continuous air sparge of one liter per minute.

Id., at 23-26; 42.

187. Figures 9 and 10 graphically illustrate the complete precipitation of zinc (white circles) and manganese (plus sign “+”) from the silica and iron free brine.

Both figures are reproduced below:

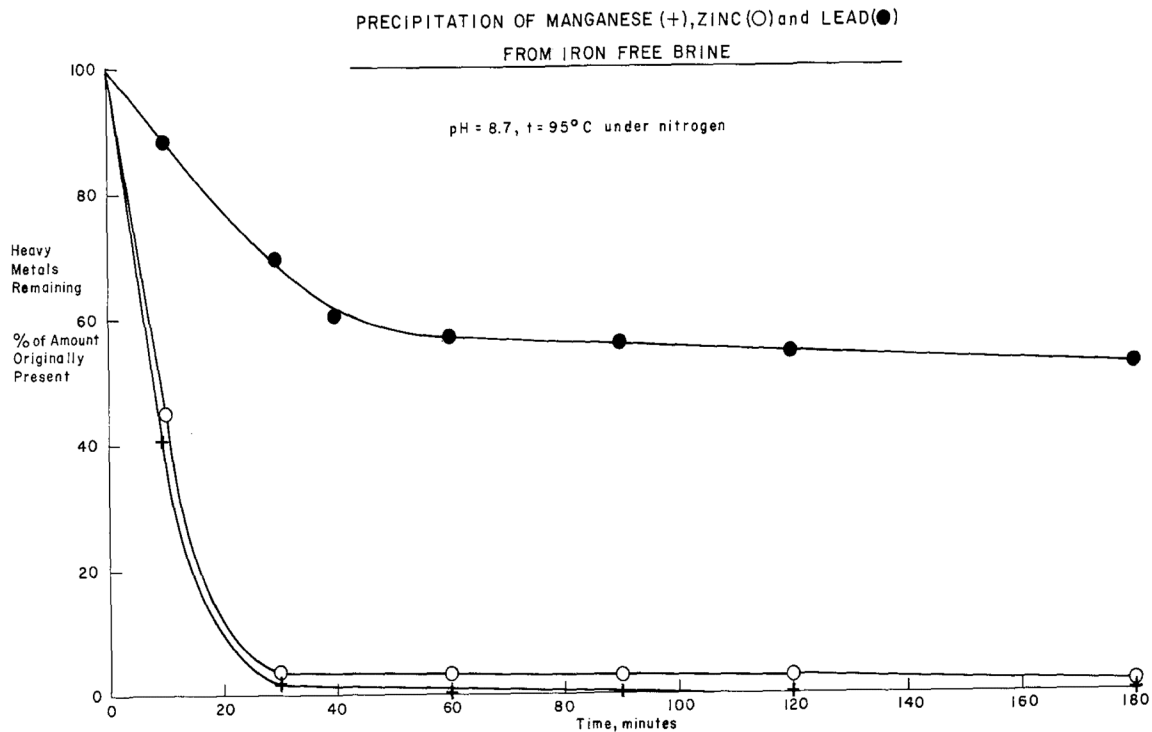


FIGURE 9
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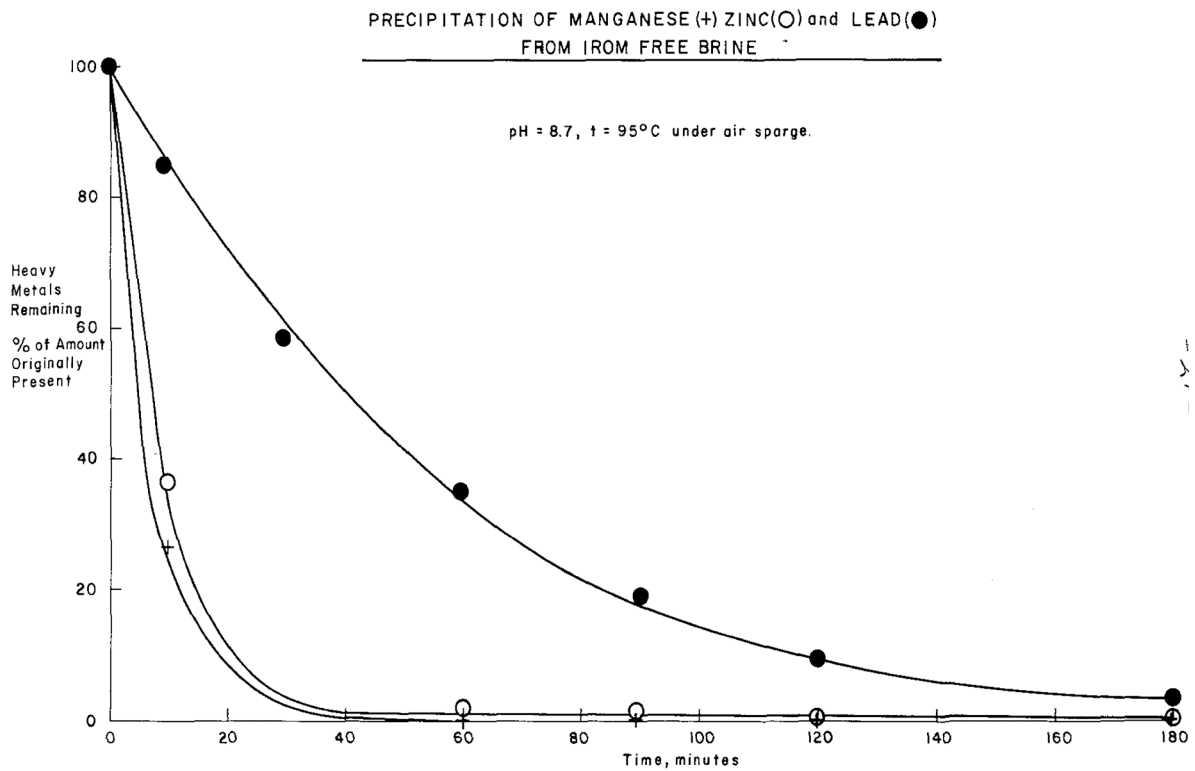


FIGURE 10
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Id., at 24-25.

188. Since iron precipitates quantitatively with silica under the oxidizing conditions shown in Figure 10, any remaining iron and silica precipitate with the complete precipitation of zinc and manganese to yield a treated geothermal brine having little to no silica, zinc and iron remaining.

189. Moreover, a POSITA could easily adjust the parameters of *Christopher* (e.g., pH ranges, oxidant type and amount, oxidation rate, etc.) to reduce the silica concentration in the pre-flash or post-flash brine down to about 5 mg/kg or less in the clarified brine. A POSITA with a treated geothermal brine composition having reduced iron, zinc and silica content similar to that disclosed in *Christopher* would readily appreciate that the brine could be reinjected into the reservoir based on its reduced scaling content and improved injectability.

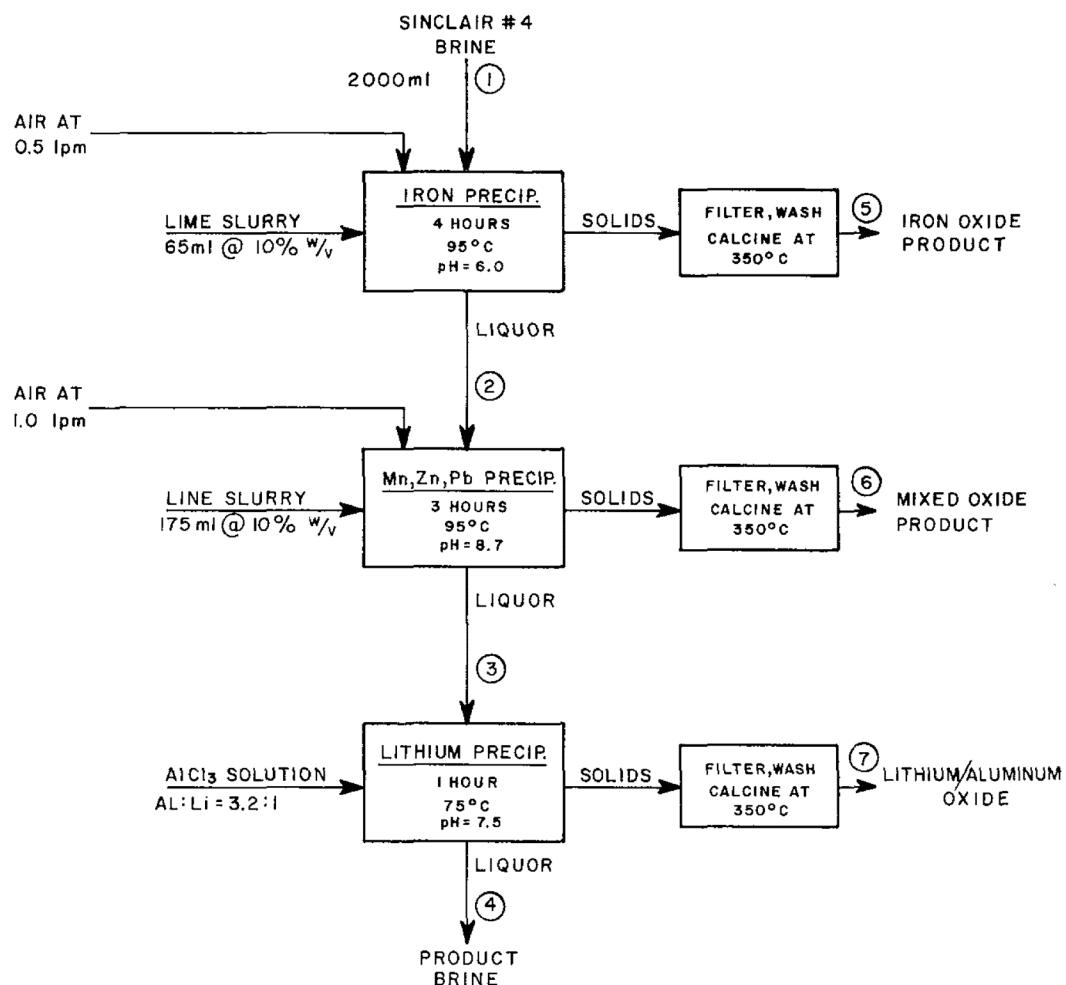
190. With the brine being sufficiently clarified by selective and sequential precipitation of silica and iron and then manganese and zinc, *Christopher* discloses the recovery of lithium. *Id.*, at 27-33. *Christopher* states that the “preferred method of recovery is based on the precipitation of lithium with aluminum hydroxide...to form an insoluble, hydrated lithium aluminate complex.” *Id.*, at 27.

191. *Christopher* conducted a series of tests to establish the optimum conditions for lithium recovery. *Christopher* obtained lithium in excess of 99% of the total

available using aluminum chloride solution and lime slurry to maintain the pH range between 6 and 8.3. *Id.*, at 28-29.

192. Lastly in Figure 20, *Christopher* discloses “a batch evaluation of the processes developed in the various sections of this report for the selective separation of iron, the remaining major heavy metals, and lithium from Sinclair No. 4 brine. Note that the final product brine has undergone further purification during lithium precipitation by virtue of the ability of aluminum hydroxide to coprecipitate the heavy metal hydroxides.” *Id.*, at 41.

FLWSHEET FOR BRINE PURIFICATION



LIQUOR	CONCENTRATION, PPM				
	Mn	Fe	Zn	Pb	Li
① FEED	2000	1810	805	120	
② IRON PRECIP. DISCH.	2000	20	780	110	
③ Mn PRECIP. DISCH.	<1.0	1.0	5.0	5.0	440
④ PRODUCT BRINE	<1.0	<1.0	<1.0	<1.0	4.6

SOLID	Wt., g.	CONCENTRATION, %				
		Mn	Fe	Zn	Pb	Li
⑤ IRON OXIDE Product	4.9	<0.1	68.0	0.9	0.4	—
⑥ MIXED OXIDE Product	8.5	47.3	0.6	18.2	2.8	—
⑦ LITHIUM/ALUMINUM Oxide	—	—	—	—	—	3.7

FIGURE 20
hri

Id., at 42.

d. U.S. Patent No. 6,517,701, for “Lead, Zinc, and Manganese Recovery from Aqueous Solutions”, to Geisler, filed August 14, 2001, and issued Feb. 11, 2003.

193. I have reviewed *Geisler* in connection with the instant IPR.

194. *Geisler* was not of record, nor was it considered, during the prosecution of the ‘117 patent.

195. *Geisler* issued February 11, 2003, from an application filed August 14, 2001. EX 1009. As such, *Geisler* is prior art under 35 U.S.C. § 102(b).

196. *Geisler* is directed toward recovery of lead, zinc and manganese from aqueous solutions or leachate by sequential solvent extraction. EX 1009, Abstract.

197. *Geisler* is from the same field of endeavor as that of the ‘117 patent as it deals with aqueous solutions or leachate that contain concentrations of lead, zinc, and manganese plus other alkaline earth metals in solution. *Id.*, 4:23-28. A POSITA who sought to solve the problem set out in the ‘117 patent would find *Geisler* to be of particular relevance.

198. *Geisler*’s leachate is a “brine” as that term is defined in the ‘117 patent, “... brine refers to any aqueous solution that contains a substantial amount of dissolved metals, such as alkali and/or alkaline earth metal salt(s) in water ...”. EX 1001, 5:54-57; *accord*: “Generally, brines suitable for the methods described herein are aqueous solutions that may include alkali metal or alkaline earth chlorides, bromides, sulfates, hydroxides, nitrates, and the like, as well as natural brines. In certain brines,

metals may be present.” *Id.*, 5:61-65. This includes “industrial brines recovered from ore leaching, mineral dressing, and the like.” *Id.*, 6:9-11.

199. The process taught in *Geisler* uses sequential solvent extraction to remove lead, zinc and manganese, among others, after removal of interfering metals. EX 1009, Abstract.

200. *Geisler* discovered that lead, zinc, and manganese can be “selectively recovered from aqueous solutions or leachate” with essentially no other metallic impurities. *Id.*, 2:51-55.

201. *Geisler* summarizes one embodiment in pertinent part as follows:

(a) extracting the aqueous solution at a pH of from 0.0 to 0.5 with an organic phase comprising substituted monothiophosphinic acid to extract lead;

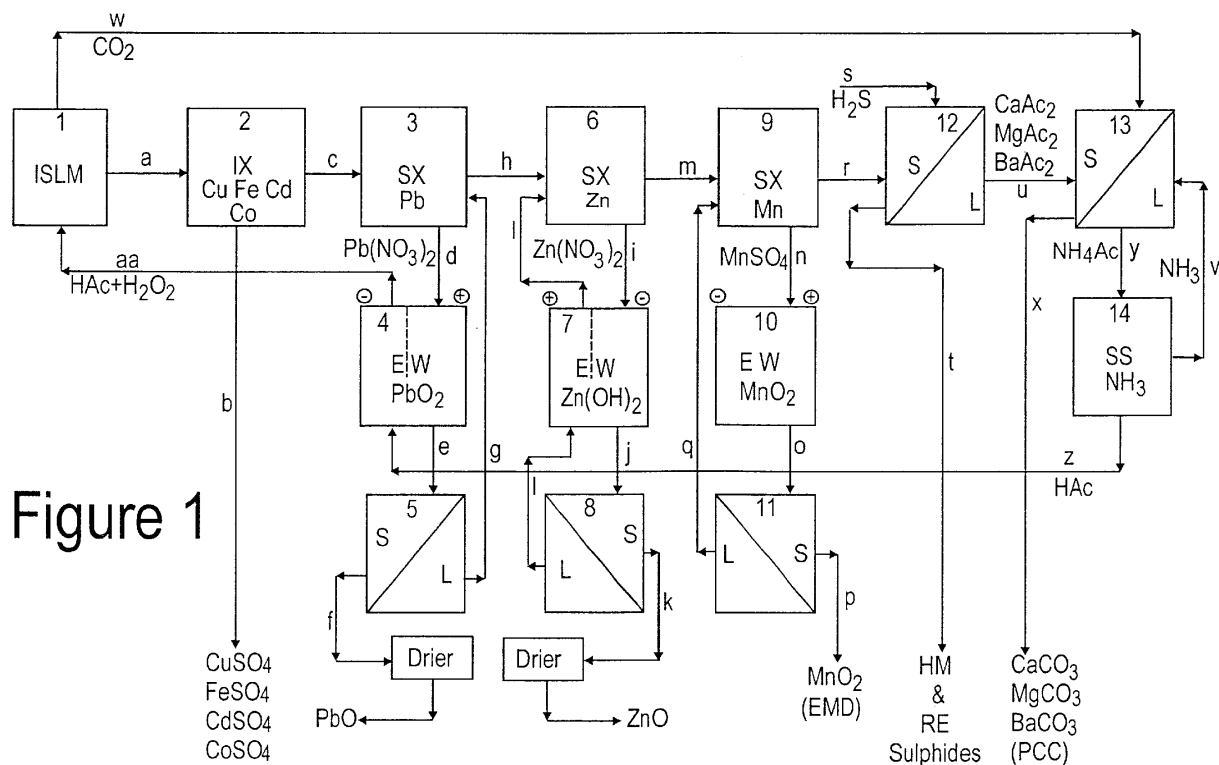
(b) extracting the lead-free aqueous solution at a pH of from 1.0 to 1.2 with an organic phase comprising at least one of substituted monothiophosphinic acids, disubstituted-phosphoric and -phosphorothioic acids, and CHSNO known as LIX 34™ **to extract zinc**;

(c) extracting the lead- and zinc-free aqueous solution at a pH of from 3.0 to 3.5 with an organic phase comprising at least one of substituted monothiophosphinic acids, disubstituted phosphinic acids, and disubstituted phosphoric and -phosphorothioic acids **to extract manganese**;

Id., 3:48-62, emphasis added.

202. Any interfering metals, such as iron, are removed by ion exchange in *Geisler* prior to solvent extraction. *Id.*, at Abstract, Figure 1.

203. Figure 1 of *Geisler* is reproduced below:



204. “As described below the presence of ... iron has been found to interfere with extraction when using mono-thiophosphinic acids by degrading the extractant. ... These interfering metals are removed before extraction e.g. by ion exchange.” *Id.*, 5:1-7.

205. *Geisler* used the commercial product Cyanex 302 to selectively recover zinc and manganese from the leachate. Cyanex 302 is an organic extractant bis(2,4,4-trimethylpentyl)-monothiophosphinic acid with the molecular formula $(C_8H_{17})_2P(S)OH$, and is described in U.S. Patent No. 5,028,403, which is incorporated herein by reference. *Id.*, 5:45-50.

206. *Geisler* states that his “invention initially removes when present, Cu and Fe from the leachate, e.g. by means of an ion exchange (IX) resin or precipitation, to prevent Cyanex 302 degradation and further removes any Cd and Co from the said leachate, e.g. also by means of IX or precipitation, to enable selective extraction of the Pb, Zn and Mn in that order from the leachate by means of the Cyanex 302 or other extractants as described.” *Id.*, 6:1-8.

207. The ‘117 patent lists this same extractant as an exemplary solvent for removing zinc. EX 1001, 9:8-31.

208. As can be seen in Figure 1 of *Geisler*, zinc and manganese are removed from the brine in separate steps via solvent extraction (*i.e.*, “SX”), Boxes 6 and 9 respectively. EX 1009.

209. The embodiment of Figure 1 Box 6 of *Geisler* (zinc extraction) uses the commercial product Cyanex 302 at a concentration of 20 wt% in kerosene to selectively recover zinc. *Id.*, 7:61-67.

210. Box 9 of that same figure uses the same commercial product Cyanex 302 at a concentration of 20 wt% applied to the zinc free stream “m” to selectively recover manganese, as MnSO_4 . *Id.*, 7:61-67.

211. *Geisler* goes on describe electrowinning at Box 10 of Figure 1. “The MnSO_4 strip liquor (n) is treated (10) at the anode of an electrolytic cell to recover about 80% of its dissolved Mn... which deposits on the anode as MnO_2 .” *Id.*, 9:20-24.

212. The solid phase (p) from the electrowinning circuit Box 10 is washed and dried. *Id.*, 9:37-40.

213. The liquid phase (q) containing MnSO₄ is recycled to:

the solvent extraction step (9) where it picks up additional Mn to become (n). The reactions are:

At the Anode



Id., 9:40-47.

214. In Example 5, *Geisler* notes that the precipitated MnO₂ are “spalled into the discharge electrolyte” at the anode of the electrowinning cell. *Id.*, 14:57-59, and recovered the dissolved Mn at the anode as MnO₂ with a purity of 99.99%. *Id.*, 14:59-62.

e. U.S. Patent No. 4,405,463, for “Process for Stabilizing Silica-Rich Geothermal Brine to Prevent Silica Scaling”, to Jost, *et al.*, filed November 4, 1981, and issued September 20, 1983.

215. I have reviewed *Jost* in connection with the instant IPR.

216. *Jost* was not of record, nor was it considered, during the prosecution of the ‘117 patent.

217. *Jost* issued September 20, 1983, from an application filed November 4, 1981. EX 1007. As such, *Jost* is prior art under 35 U.S.C. § 102(b).

218. *Jost* teaches a process for “removing silica from silica-rich geothermal brine” which is “applicable to a wide variety of applications in which removing silica from geothermal brine or other liquids is desired or required.” EX 1007, 4:7-11.

219. *Jost* is from the same field of endeavor as that of the ‘117 patent as it deals with selective removal of silica and iron from “silica-rich geothermal brines, representative of which are those found in the Imperial Valley of Southern California.” *Id.*, at Abstract and col. 2:26-28. The ‘117 patent describes its geothermal brine solutions as including “Salton Sea brines,” which are also from Imperial Valley of Southern California. The high salinity brines of the Salton Sea have concentrations of silica, iron, zinc, manganese, lithium, and other minerals and metals.

220. In my opinion, a POSITA who was seeking to selective reduce the silica and iron concentrations in geothermal brines would find the *Jost* reference to be especially relevant.

221. Furthermore, *Jost* discloses “...as is typical of many geothermal brines, the brine is presumed to be rich not only in dissolved silica, primarily amorphous silica, but also in iron, principally in the ferrous (Fe⁺²) ion state.” *Id.*, 4:40-44.

222. Since the brines produced in Imperial Valley of Southern California also include zinc, manganese, lithium and other metals and minerals, *Jost* further teaches that “the present silica removal process can be used for recovery of salts or mineral

species contained in geothermal aqueous liquids and which precipitate or are carried along with the iron-rich siliceous material precipitated by the process.” *Id.*, 4:16-20.

223. The process taught by *Jost* includes:

selectively providing a supply of ferric ions, allowing the silica-rich brine to combine with the ferric ions to form insoluble, iron-rich siliceous material and separating the insoluble siliceous material from the brine to form a brine having a silica content which is reduced below the saturation level required for substantially scale-free handling of the brine. In one embodiment of the process in which the brine contains sufficient dissolved ferrous ions, the process comprises selectively contacting the brine with an oxidizing agent, preferably by aerating the brine, to oxidize a selected portion of the ferrous ions to ferric ions, which then combine with silica to form the insoluble iron-rich siliceous material.

Id., at Abstract.

224. “[T]he process is effective for removing silica from silica-rich geothermal brine so as to provide substantially silica scale-free brine reinjection, or other disposal or use.” *Id.*, 3:16-20, emphasis added.

225. *Jost* further discloses that the process can be tuned to achieve the amount of silica removal desired, (*Id.*, 3:28-33) and “[a]ccordingly, if silica scaling, indicative of insufficient silica removal, occurs in brine effluent reinjection system 16, ferric and/or ferrous ions may be added from supply sources 174 and/or 180 until formation of silica scale ceases.” *Id.*, 9:55-59.

226. *Jost* further teaches that the process can be tuned by varying “brine temperature, pressure, pH, silica content, ferrous ion content, content of other

materials which may enhance or inhibit silica precipitation, and flow rate. Still other variables include brine effluent disposal (or use) conditions such as changes in brine temperature, pressure and pH along the disposal (or use) path and brine residence time during disposal (or use).” *Id.*, 11:4-11.

227. *Jost* discloses that the “clarified, stabilized brine, usually having a substantially reduced silica content, is discharged from tank 122 through conduit 110, to be pumped by pump 106 through conduit 112 into reinjection well 108.” *Id.*, col. 9:3-8. *Jost* also discloses in an example that within the clarifier tank (122), “the brine effluent is found to have the following approximate ranges of characteristics:

Temperature, °F.	160 to 200
pH,	3 to 5
Silica Content, ppm	90 to 150
Ferrous ion content, ppm	2000 to 3000
Ferrie ion content, ppm	5 to 60

Id., col. 11 line 67-12:10. Additionally, *Jost* calls for a “maximum dissolved silica level” that “is below 150 ppm.” *Id.*, col. 13:20-22.

228. Therefore, it is clear to a POSITA that *Jost* contemplates removing enough silica through its selective removal process to produce a “substantially silica free brine” that permits “substantially silica scale-free brine reinjection”.

f. U.S. Patent No. 4,016,075, for “Process for Removal of Silica From Geothermal Brine”, to Wilkins, *et al.*, filed March 17, 1975, and issued April 5, 1977.

229. I have reviewed *Wilkins* in connection with the instant IPR.

230. *Wilkins* was cited in an IDS by the patent examiner, but was not otherwise considered during the prosecution of the ‘117 patent.

231. *Wilkins* issued April 5, 1977, from an application filed March 17, 1975. EX 1008. As such, *Wilkins* is prior art under 35 U.S.C. § 102(b).

232. In my opinion, a POSITA who was seeking to reduce the silica concentration in geothermal brines would find the *Wilkins* reference to be especially relevant.

233. *Wilkins* is from the same field of endeavor as that of the ‘117 patent, *i.e.*, recovery of minerals and metals from geothermal brines, including, specifically, geothermal brines from the Salton Sea. EX 1008, 1:6-12.

234. *Wilkins* is directed at a process for the removal of silica from geothermal brines found in Imperial County, California. *Id.*, Title, 1:6-9.

235. *Wilkins* notes that “typical samples of the geothermal brine have been analyzed and found to contain, on average, the following solids dissolved therein:”

	Concentration in mg/l
Sodium	69,700
Potassium	16,400
Lithium	200
Calcium	30,600
Iron	1,400
Manganese	1,600
Lead	100
Magnesium	80
Silver	nil
Zinc	360
Copper	3
Barium	1,300
Strontium	580
Aluminum	95
Ammonium (NH ₄)	400
Fluoride	450
Chloride	148,400
Boron	180
Sulfate (SO ₄)	130
Silica (SiO ₂)	860
Total dissolved solids	~272,900

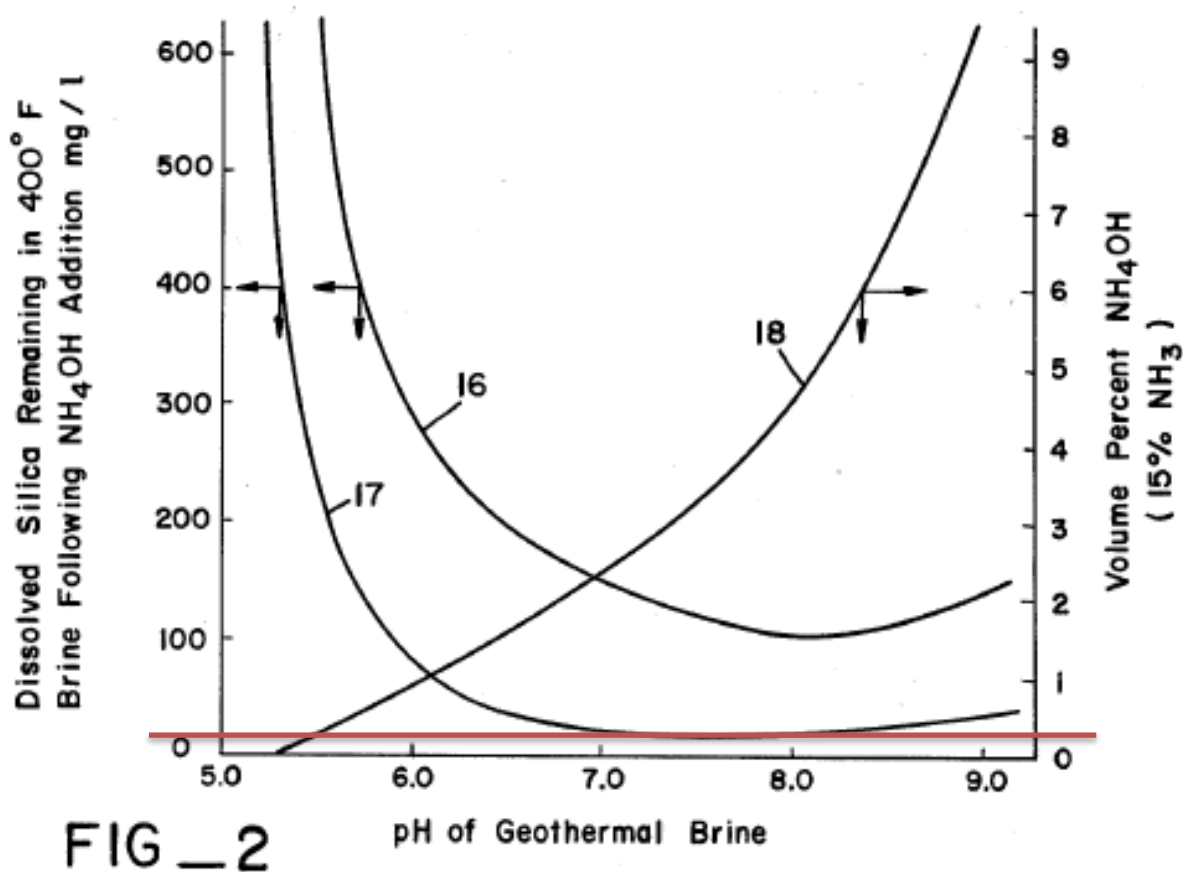
Id., 1:4-41.

236. *Wilkins* discloses the creation of a “gelatinous sludge precipitate of aluminum and ferrous hydroxides.” *Id.*, 2:43-46. *Wilkins* further explains that “[i]f desired, a portion of the brine and sludge may be recycled back to the reaction chamber 13 through line 24, the sludge being lanced with air to oxidize the ferrous hydroxide to ferric hydroxide. The injection of ferric hydroxide into reaction chamber 13 will modify the precipitate formed in the reaction chamber, forming a mixture of ferrous and ferric hydroxides in the sludge that will make the sludge less gelatinous and therefore less likely to stick on equipment surfaces.” *Id.*, 5:46-54 and Figure 1. *Wilkins* continues by noting that the “precipitated sludge formed in the brine will

‘sweep’ the brine so that dissolved silica will adsorb on the surface of the sludge particles.” *Id.*, 2:46-49.

237. In this way, *Wilkins* teaches forming iron (III) hydroxide, injecting the iron (III) hydroxide into the reaction chamber (13) and then contacting the silica with iron (III) hydroxide for a time sufficient for the dissolved silica to “adsorb on the surface of the sludge particles.”

238. *Wilkins* further discloses in Figure 2 (reproduced below) “the relationship between brine pH and the amount of silica remaining in brine at 400° F. when ammonium hydroxide is added to the brine. The upper and lower curves 16 and 17 represent boundary lines for points established empirically during static tests of this relationship. It has been found through experience that the lower curve 17 more nearly represents the relationship during dynamic operation wherein brine and ammonium hydroxide continuously pass into and through reaction chamber 13 during normal production from the well.” *Id.*, 4:1-11.



239. As can be seen from Figure 2 of *Wilkins* and the corresponding written description, based at the pH range of the geothermal brine (*i.e.*, between 5.0 and 8.0), the dissolved silica in the geothermal brine is reduced by more than 90% relative to the feed brine using ammonium hydroxide.

240. *Wilkins* also discloses reinjecting the clarified brine filtrate in a brine disposal well (26). *Id.*, 5:55-56; Figure 1.

241. *Wilkins* also teaches that the treated geothermal brines can be further processed for mineral recovery, such as manganese recovery. *Id.*, 2:9-11 and lines 64-68.

g. U.S. Patent No. 5,358,700, for “Method of Extracting Zinc from Brines”, to Brown, *et al.*, filed October 5, 1992, and issued October 25, 1994.

242. I have reviewed *Brown* in connection with the instant IPR.

243. *Brown* was not of record, nor was it considered, during the prosecution of the ‘117 patent.

244. *Brown* issued October 25, 1994, from an application filed October 5, 1992. EX 1010. As such, *Brown* is prior art under 35 U.S.C. § 102(b).

245. In my opinion, a POSITA who was seeking to reduce the silica concentration in geothermal brines would find the *Brown* reference to be especially relevant.

246. *Brown* teaches a “method of extracting zinc from geothermal brines, *e.g.*, from the Salton Sea area” (*Id.*, at Title and 4:26-27), “which contains salts of sodium, potassium and calcium chlorides, as well as a number of other elements including manganese, iron, lead, silver, magnesium, strontium and lithium.” *Id.*, 2:32-35.

247. *Brown* is from the same field of endeavor as that of the ‘117 patent as it deals with treating brines to reduce the concentration of at least one metal or elemental component, namely silica. In my professional opinion, a POSITA who was seeking to solve the problem set out in the ‘117 patent would find the *Brown* reference to be especially relevant.

248. *Brown* discloses removing “substantially all silica” from a geothermal brine before contacting the brine with an organic solvent that extracts zinc, iron and manganese therefrom. *Id.*, 4:30-47.

249. *Brown* recognizes that silica present in the brine will precipitate when flashed (*Id.*, 3:43-50), and states:

Where the brine to be subjected to the process of this invention is geothermal, the first step of the process of this invention involves removing the insoluble amorphous silica precipitate from the brine. The silica solids which have precipitated in the brines as a result of cooling and loss of acid gases are desirably removed from the brines prior to the solvent extraction process. Their removal can be achieved through careful and efficient liquid-solid separation techniques.

Id., 3:51-59.

250. *Brown* discloses “[t]he resulting pooled brine, which is now substantially free of colloidal silica, is used as the starting material for the zinc removal process. The term ‘substantially free of colloidal silica’ is defined as containing residual amounts of silica of less than 10 ppm. More preferably, the silica content remaining in the pooled brine is in the range of between about 1 to about 10 ppm SiO₂.” *Id.*, 3:60-66.

251. “The brine, removed of silica, can optionally be reintroduced into the well from which the geothermal brine was tapped. Without its removal, the costly wells are quickly plugged.” *Id.*, 3:67-4:2.

h. U.S. Patent No. 6,458,184, for “Recovery of Zinc from Geothermal Brines”, to Featherstone, filed December 20, 2000, and issued October 1, 2002.

252. I have reviewed *Featherstone I* in connection with the instant IPR.

253. *Featherstone I* was cited in an IDS, but was not otherwise considered during the prosecution of the ‘117 patent.

254. *Featherstone I* issued October 1, 2002, from an application filed December 20, 2000. EX 1011. As such, *Featherstone I* is prior art under 35 U.S.C. § 102(b).

255. In my opinion, *Featherstone I* is from the same field of endeavor as that of the ‘117 patent as it deals with removal of zinc from geothermal brines, and a POSITA who was seeking to remove zinc from geothermal brines using ion exchange and solvent extraction would find *Featherstone I* to be especially relevant.

256. *Featherstone I* was admitted as prior art in the specification of the ‘117 patent, and discloses “recovery of zinc from geothermal brines” (EX 1011, Title) using an anionic ion exchange resin (IX) followed by a water-immiscible cationic organic solvent (SX). *Id.*, Abstract.

257. *Featherstone I* teaches that:

In the case where the brine is high in silica, the brine is also preferably clarified prior to use in the instant method. ... Silica particles are added to the brine as “seed crystals.” These promote the formation of silica particles..., thereby reducing the quantity of silica in the brine. Silica particles are preferably removed before the brine is subjected to the methods of the invention.

EX 1011, 3:41-42.

258. The clarified brine is then passed over an ion exchange resin that binds zinc. *Id.*, 2:14-15; 4:18-19.

259. Iron and other contaminating metals are removed from the zinc-rich eluate by oxidation, after which zinc is removed using a solvent extraction process with an organic solvent, such as phosphoric acid (D2EHPA). *Id.*, 2:19-24; 6:56-59; 7:25-31.

i. U.S. Patent Publication No. 2003/0226761, for “Process for Producing Electrolytic Manganese Dioxide from Geothermal Brines”, to Featherstone, *et al.*, filed May 31, 2002, and published December 11, 2003.

260. I have reviewed *Featherstone II* in connection with the instant IPR.

261. *Featherstone II* was cited in an IDS, but was not otherwise considered during the prosecution of the ‘117 patent.

262. *Featherstone II* published December 11, 2003, from an application filed May 31, 2002. EX 1012. As such, *Featherstone II* is prior art under 35 U.S.C. § 102(b).

263. In my opinion, *Featherstone II* is from the same field of endeavor as that of the ‘117 patent as it deals with extraction of manganese from geothermal brines, and a POSITA who was seeking to extract manganese from geothermal brines using solvent extraction and electrowinning to produce electrolytic manganese dioxide would find *Featherstone II* to be especially relevant.

264. *Featherstone II* was admitted as prior art in the specification of the ‘117 patent, and discloses a “process for producing electrolytic manganese dioxide from geothermal brines” (EX 1012, Title), and more particular “a liquid-liquid extraction

method for separating manganese dioxide from brine using an electrolytic process.”
Id., [0001].

265. In Figure 5, *Featherstone II* discloses iron can be removed from the geothermal brine prior to solvent extraction. *Id.*, [0104]. “The iron depleted brine solution is then routed to QL loading where manganese ... [is] loaded onto the organic.” *Id.*

266. The QL reagent of *Featherstone II* is an organic solvent, “preferably diethylhexylphosphate (DEPHA)” (*Id.*, [0032]) or a Cyanex extractant. *Id.*, [0057].

267. Manganese and iron are extracted from the geothermal brine solution onto the organic phase, and then stripped with an acid such that the manganese and iron shift from the organic phase to an aqueous phase. The iron is then oxidized, and iron precipitates leaving a supernatant containing manganese. The supernatant containing manganese is then oxidized in an electrowinning cell such that electrolytic manganese dioxide is precipitated therefrom onto the anode of the electrolysis cell. *Id.*, [0022].

268. During electrowinning, manganese dioxide is deposited in the form of a dense precipitate layer at the anode. *Id.* [0084].

269. “Following the electrowinning step, the manganese dioxide product deposited on the anode is optionally finished to produce a commercial product. ... The manganese dioxide may then be removed using mechanical forces such as agitation,

flexing, scraping, etc. Finally, the manganese dioxide may be ground, milled and neutralized using known methods.” *Id.*, [0086].

270. “The final manganese produce is preferably comprised of at least 99% pure manganese dioxide.” *Id.* [0088].

VIII. DETAILED INVALIDITY ANALYSIS

271. I have been asked to provide my opinion as to whether the Challenged Claims of the ‘117 patent would have been obvious in view of the prior art. The discussion below provides a detailed analysis of how the prior art references I reviewed teach the limitations of the Challenged Claims of the ‘117 patent.

272. As part of my analysis, I have considered the scope and content of the prior art and any potential differences between the claimed subject matter and the prior art. I conducted my analysis as of the earliest claimed priority date of the ‘117 patent, *i.e.*, June 29, 2011. I have also considered the level of ordinary skill in the pertinent art as of that date. I have assumed, for purposes of this declaration only, that every claim of the ‘117 patent is entitled to this priority date.

273. I describe in detail below the scope and content of the prior art, as well as any differences between the claimed subject matter and the prior art, on an element-by-element basis for each Challenged Claims of the ‘117 patent. This analysis supports my finding that the differences between the Challenged Claims of the ‘117 patent and the prior art discussed herein are such that the subject matter as a whole would

have been anticipated and/or obvious at the time of the filing of the '117 patent to a POSITA to which the subject matter pertains.

274. As described in detail below, the claimed subject matter of the Challenged Claims would have been anticipated and/or obvious in view of the teachings of the identified prior art references as well as the knowledge of a POSITA.

275. As acknowledged in the background of the '117 patent, it was well known at the time of the invention to remove silica and extract minerals from geothermal brines (EX 1001, 1:33-53), and the prior art is replete with patents and publications that disclose the recovery of mineral values from geothermal brines. In addition, it was widely known to remove silica and iron as an initial impurity removal processing step to prevent scaling and fouling, and that a clarified brine is essential to downstream mineral recovery processing. Moreover, it was widely known during mineral recovery operations to remove zinc and extract manganese from the clarified brine.

276. The '117 patent fails to explain or even suggest why the claimed methods of recovering zinc and manganese are novel or nonobvious over conventional processing of ores and brines that have been long employed in the Imperial Valley, California and elsewhere. Without claim limitations drawn to specific, important or critical steps, the Challenged Claims simply describe known processes for impurity

removal from geothermal brines to produce a clarified brine for subsequent mineral recovery.

277. The impurity removal methods of *Maimoni*, *Christopher*, *Brown*, *Jost* and/or *Wilkins* provide a clarified brine that is substantially free of silica and iron, which is suitable for use with the mineral extraction methods of *Maimoni* (precipitation) and/or *Christopher* (precipitation) and/or *Bourcier* (ion exchange and solvent extraction) and/or *Geisler* (solvent extraction and electrowinning) and/or *Brown* (solvent extraction).

278. I will now describe on an element-by-element basis how the prior art teaches all of the elements of Claim 12. Unless otherwise noted, all italics, and bold italics emphasis in any quoted material has been added.

279. *Maimoni* is directed to “A Cementation Process for Minerals Recovery from Salton Sea Geothermal Brines”. EX 1004, Title. *Maimoni* details the selective precipitation of metal hydroxides from Magmamax No. 1 geothermal brine using lime. *Id.*, at 14. Figure 5 and Table 5 of *Maimoni* detail a method for recovering zinc and manganese from Magmamax No. 1 geothermal brine. *Id.*, at 15-17.

280. *Maimoni* discloses providing a geothermal brine that contains manganese and zinc. *Id.*

281. Stream 1 of *Maimoni* provides the Magmamax No. 1 geothermal brine having manganese and zinc to a silica reactor. *Id.*

	1
SiO ₂	230 ppm total 187 ppm solid
Fe	255 ppm
Zn	333 ppm
Mn	775 ppm
Pb	70 ppm
Li	182 ppm
Inertia	22.1%
H ₂ O	77.7%
Specific grey	1.135
Temp. °C	93
Temp. °F	200
Flow, gpm	15
Flow, gph	900
Flow, cfm	—
Flow, lb/h	8523
Specific heat Btu/lb °F	0.85
Heat Btu/h	1.45 × 10 ⁶
Density	9.47 lb/gal
NH ₃	352 ppm

Id., at 16, highlighting added.

282. *Maimoni* discloses selectively removing silica and iron to produce a substantially silica free brine having manganese and zinc. *Id.*, 15-17.

283. *Maimoni* selectively removes silica from the geothermal brine between Streams 1 and 4, and further selectively removes silica and iron between Streams 4 and 11. *Id.* Streams 1, 4 and 11 of Table 5 are reproduced below for comparison:

	1		4		11
SiO ₂	230 ppm total 187 ppm solid		43 ppm		22 ppm
Fe	255 ppm		255 ppm		26 ppm
Zn	333 ppm		333 ppm		333 ppm
Mn	775 ppm		775 ppm		775 ppm
Pb	70 ppm		70 ppm		56 ppm
Li	182 ppm		182 ppm		182 ppm
Inertia	22.1%		22.1%		22.1%
H ₂ O	77.7%	• • •	77.7%	• • •	77.1%
Specific grey	1.135		1.135		1.13
Temp. °C	93		93		92
Temp. °F	200		200		198
Flow, gpm	15		15		15
Flow, gph	900		900		901
Flow, cfm	—				
Flow, lb/h	8523		8520		8508
Specific heat Btu/lb °F	0.85		0.85		0.85
Heat Btu/h	1.45 × 10 ⁶		1.45 × 10 ⁶		144 × 10 ⁶
Density	9.47 lb/gal		9.47 lb/gal		944 lb/gal
NH ₃	352 ppm		352 ppm		352 ppm

Id., highlighting added.

284. Consequently, *Maimoni* selectively removes silica and iron from the geothermal brine as that phrase is used in the ‘117 patent.

285. The concentration of silica in the brine was reduced by about 90% from 230 ppm to 22 ppm between Stream 1 and Stream 11. EX 1004, at 16. Similarly, the concentration of iron in the brine was reduced by about 90% from 255 pm to 26 ppm between Streams 1 and 11, and the substantially silica free brine of Stream 11 includes 333 ppm of zinc and 775 ppm of manganese. *Id.*

286. In my opinion, the treated geothermal brine of *Maimoni* in Stream 11 is a “substantially silica free brine” as that phrase is used in the ‘117 patent.

287. Just as is taught in *Maimoni*, each of the embodiments of Figures 1-11 and Examples 1-3 of the ‘117 patent selectively remove silica and iron from the brine by oxidizing the ferrous iron to ferric iron by sparging the brine with air and using calcium hydroxide to control the pH of the brine.

288. Similar to the ‘117 patent and *Christopher*, when the iron in Stream No. 11 is further oxidized with air from Stream No. 13, any ferrous, Fe^{2+} , iron is oxidized and converted into the ferric ion; and the Fe^{3+} reacts quantitatively with silica to form insoluble ferric silicate precipitate.

289. By oxidizing the iron in the iron reactor with air (Stream 6), the pH of the brine in the iron reactor is generally reduced. The reduction of the pH is offset by the introduction of calcium hydroxide (Stream 5) to the iron reactor.

290. *Maimoni* describes a step of maintaining and controlling the pH of the geothermal brine at an adjusted pH of between 4.5 and 6.5. Given the pH of the feed brine, these pH values occur as a result of the air oxidation and introduction of calcium hydroxide.

The ferric hydroxide and silica coprecipitate in the iron reactor and iron thickener. A slipstream of the ferric hydroxide and silica precipitate slurry is recycled back to Stream 1 to provide “seed” to the silica reactor. EX 1004, at 15.

291. Thus, *Maimoni* selectively removes silica and iron from the geothermal brine by “providing iron (III) at a pH of between about 4.5 and 6 and precipitating the silica.”

292. Accordingly, *Maimoni* reduces the iron concentration is reduced by about 95% in in Stream Nos. 18, 21 and 24, and similarly, the silica concentration is inherently reduced by about 95% in s in Stream No. 18, 21 and 24 of *Maimoni*.

293. A POSITA would appreciate that the 22 ppm of silica in Stream No. 11 of *Maimoni* coprecipitates with the 26 ppm of iron based on the disclosed processing conditions, and as such, the concentration of silica is reduced well below the reported 22 ppm.

294. When *Maimoni* adds $\text{Ca}(\text{OH})_2$ and aerates Salton Sea geothermal brine, ferric silica solid precipitates and the concentration of iron reacts with the silica in the geothermal brine to reduce the silica concentration by about 95%. By maintaining the pH of the brine with lime or caustic soda or ammonia, the iron precipitates quantitatively to yield a brine with low iron and silica concentrations (*e.g.*, iron concentrations reduced by about 95% in Streams 18, 21 and 24).

295. A POSITA would further appreciate that by adding additional caustic soda and controlling the pH, the process could be tuned such that silica and iron are completely removed from the Salton Sea geothermal brine.

296. In my professional opinion, the process taught by *Maimoni* (the addition of pH control with lime and air sparging) will selectively remove silica and iron to produce a substantially silica free brine as that phrase is used in the '117 patent.

297. The “substantially silica free brine” also contains reported amounts of zinc and manganese that remain unchanged as the silica and iron are selectively removed from the brine. *Id.*, at Table 5, Stream 15.

298. *Maimoni* teaches removing zinc from the substantially silica free brine by precipitation. Zinc is precipitated from the geothermal brine by using air and lime. In Table 5, the zinc amount is seen to have been reduced from 333 ppm in the iron thickener overflow (Stream 11) to 17 ppm in the manganese thickener overflow (Stream 18). Streams 11, 15 and 18 of Table 5 are reproduced below for comparison:

	1		11		15		18
SiO ₂	230 ppm total 187 ppm solid		22 ppm				
Fe	255 ppm		26 ppm		26 ppm		13 ppm
Zn	333 ppm		333 ppm		333 ppm		17 ppm
Mn	775 ppm		775 ppm		775 ppm		39 ppm
Pb	70 ppm		56 ppm		56 ppm		6 ppm
Li	182 ppm		182 ppm		182 ppm		182 ppm
Inertia	22.1%		22.1%		22.1%		22.1%
H ₂ O	77.7%		77.1%		77.7%		77.8%
Specific grey	1.135	• • •	1.13	• • •	1.132	• • •	1.13
Temp. °C	93		92		90		90
Temp. °F	200		198		195		195
Flow, gpm	15		15		15		15
Flow, gph	900		901		904		902
Flow, cfm	—						
Flow, lb/h	8523		8508		8540		8515
Specific heat Btu/lb °F	0.85		0.85		0.85		0.85
Heat Btu/h	1.45 × 10 ⁶		144 × 10 ⁶		1.41 × 10 ⁶		1.41 × 10 ⁶
Density	9.47 lb/gal		944 lb/gal		9.45 lb/gal		9.44 lb/gal
NH ₃	352 ppm		352 ppm		352 ppm		35 ppm

Id., at 16-17, highlighting added.

299. In my opinion, *Maimoni* teaches “removing the zinc from the substantially silica free brine” by precipitation.

300. *Maimoni* teaches removing manganese from the substantially silica free brine. Manganese is precipitated from the geothermal brine by using air and lime. In Table 5, the manganese amount is seen to have been reduced from 775 ppm in the iron thickener overflow (Stream 11) to 39 ppm in the manganese thickener overflow (Stream 18).

301. In my opinion, *Maimoni* teaches “extracting manganese from the substantially silica free brine” by precipitation.

302. *Bourcier* discloses a method for recovering metals including zinc and manganese from geothermal brines: “This paper discusses the opportunities, the processes, the challenges, the current status, the economics and the potential for recovery of minerals and metals from geothermal fluids.” EX 1005, at Title and Abstract.

303. *Bourcier* discloses providing a geothermal brine with manganese and zinc:

The geothermal waters have had intimate and lengthy contact with the layers of the earth’s crust that they flow through, resulting in dissolution of minerals and metals from the rocks, and solution into the hot water. These aqueous solutions can be processed to recover minerals and metals. Potential products include silica, zinc, lithium, and other materials. Recovery of minerals and metals from geothermal fluids can be viewed as “solution mining by nature”, followed by application of established or new hydrometallurgical techniques for isolation and purification.

Id., at Abstract.

304. *Bourcier* also discloses that the Salton Sea geothermal brines are “unique in having extremely high salinity and a high base metal content. The fluid is especially enriched in metals that form strong hydrothermal complexes with chloride, such as zinc, copper, lead and silver.” *Id.* at 13. *Bourcier* goes on to disclose various recovery processes for recovering zinc and manganese from these metal-rich (Salton Sea and other) geothermal brines. *Id.*, at 11-12.

305. *Bourcier* teaches selectively removing silica and iron from the geothermal brine by precipitation to produce a substantially silica free brine that contains manganese and zinc.

306. *Bourcier* recognizes the importance of *removing* silica before attempting to recover manganese and zinc:

Silica must be removed from the fluid for the zinc extraction process to be successful. If not, the ion exchange resins are quickly covered by silica precipitates and fail to efficiently extract zinc. The silica is currently removed upstream using a clarification process that combines lime addition and silica seeding.

Id., at 12, emphasis added; *accord*: “Silica is an ubiquitous component of geothermal fluids and must be removed or reduced in concentration to allow other components to be removed.” *Id.*, at 4.

307. Since silica and iron are known to coprecipitate, the silica removal step of *Bourcier* will also inherently precipitate iron. “The silica precipitated with this method has significant amounts of contaminants such as iron ...”. *Id.*

308. In my professional opinion, the process taught by *Bourcier* (the addition of pH control with lime and silica seeding) will selectively remove silica and iron to produce a substantially silica free brine as that phrase is used in the ‘117 patent.

309. The substantially silica free brine includes manganese and zinc, which can then be recovered. *Id.*, at 11-13.

310. *Bourcier* teaches removing zinc from the substantially silica free brine. The zinc is said to be removed by ion exchange and solvent extraction. “Separation using commercial ion-exchange resins has been used to recover zinc from high salinity brines (see Salton Sea case history below).” *Id.*, at 4; *see also*:

The metal-rich geothermal fluids are being mined for their zinc content by CalEnergy Minerals. Their process utilizes 105°C “spent brine” downstream from the steam separation and energy extraction processes. The brine is passed over an anionic ion exchange bed (IX) to extract the zinc present in the fluid primarily as anionic ZnCl_4^{2-} . The resin is then eluted with an acidic solution that contains a reducing agent. Iron, arsenic and lead are also extracted in the process, but are subsequently removed by oxidation followed by solids removal. The zinc is then extracted from the eluate in a solvent extraction process (SX) utilizing a water immiscible cationic extractant. After removal of the zinc-depleted aqueous phase, the zinc-loaded SX extractant is rinsed and then stripped with a sulfuric acid solution. After separation of the SX extractant, the zinc sulfate solution undergoes electrowinning to produce metallic zinc.

Id., at 11-12, emphasis added.

311. As noted above, *Bourcier* acknowledges that the presence of silica will frustrate the zinc removal process. As such, silica must have been removed beforehand in order for the mineral recovery process to operate successfully.

312. *Bourcier* discloses extracting manganese from the substantially silica free brine by solvent extraction.

CalEnergy has investigated methods for extracting manganese from their brines. The targeted by-product is electrolytic manganese dioxide for use in batteries. ... Preliminary work shows that a solvent extraction method utilizing diethylhexyl phosphoric acid and a quaternary amine shows good selectivity for manganese over other metals present in the

brine. More work on manganese extraction is anticipated subsequent to successful full-scale zinc extraction.

Id., at 11.

313. As such, *Bourcier* teaches producing manganese dioxide by electrolytic deposition.

314. *Bourcier* discloses extracting manganese *subsequent to* removal of zinc, which requires as a prerequisite removal of silica.

315. *Christopher* discloses “The Recovery and Separation of Mineral Values from Geothermal Brines”. EX 1006, Title. “The subject laboratory process study on recovery and separation of minerals from Sinclair No. 4 geothermal brines developed methods for recovering iron and manganese hydrated oxide compounds as separate components, essentially quantitatively. In addition, lead and zinc values were also removed, essentially quantitatively, as co-precipitated compounds together with the hydrated manganese oxides.” *Id.*, at 6.

316. *Christopher* discloses providing a geothermal brine that contains manganese and zinc. *Id.*, at 8. *Christopher* provides the post-flash geothermal brines for heavy metal precipitation in Table 3 that include zinc and manganese, and for sequential brine purification in Figure 20. *Id.*, at 12, 42.

317. *Christopher* teaches selectively removing silica and iron from the geothermal brine by precipitation to produce a substantially silica free brine that contains manganese and zinc.

318. *Christopher* flashes the Sinclair No. 4 brine and that process decreases the silica concentration from an initial value of 750 ppm (*Id.*, at 12-13) down to 40 ppm (Table 1, p. 12), which amounts to an approximate 95% reduction in silica in the post-flash brine relative to the feed brine.

319. Thus, *Christopher* teaches removing silica to produce a substantially silica free brine.

320. *Christopher* goes on to selectively remove iron from the post-flash brine by precipitation of ferrous hydroxide or by oxidizing the brine under controlled pH conditions to produce an “iron free brine”. EX 1006, at 16-22 and 42.

321.

322. *Christopher* also teaches that iron is selectively precipitated and separated from the post-flash brine by precipitation of ferrous hydroxide or from the oxidizing lime (Figure 4) or ammonia (Figure 5) slurry to control pH between 5.5 and 7 in order to produce an “iron free brine”. *Id.*, at 20-27, and 46.

323. “At pH = 6, 97% of the iron has been removed from solution with essentially no loss of manganese, zinc, and lead.” *Id.*; see also Figure 6.

324. Figure 20 of *Christopher* also discloses an iron concentration in the Feed Brine (1) of 1810 ppm, which is reduced to 20 ppm in the Iron Precipitation Discharge Liquor (2). Figure 20 of *Christopher* also discloses concentrations of

manganese and zinc in the Iron Precipitation Discharge Liquor (2), which remain relatively unchanged from the Feed Brine (1). *Id.*, at 46.

325. Like *Christopher*, the embodiments of Figures 1-11 and Examples 1-3 of the '117 patent all selectively remove silica and iron from the brine by oxidizing the ferrous iron to ferric iron by sparging with air and controlling the pH of the brine using calcium hydroxide/lime slurry.

326. Since silica and iron are known to coprecipitate together, the iron removal step of *Christopher* will also inevitably precipitate silica.

327. In my professional opinion, the process taught by *Christopher* (the addition of pH control between 4.5 and 6 with lime and air sparging) will selectively remove silica and iron to produce a substantially silica free brine as that phrase is used in the '117 patent.

328. In my opinion, a POSITA would appreciate that silica in the pre-flash brine and post-flash brine of *Christopher* coprecipitates with iron based on the disclosed pH and oxidizing processing conditions, thereby reducing the concentration of silica in the treated geothermal brine to well below the reported silica concentration levels.

329. When *Christopher* aerates the Sinclair No. 4 brine and maintains the pH of the brine with lime, iron reacts quantitatively with silica to form a ferric silicate precipitate, and the silica and iron concentrations reduced by at least 95% in the

Product Brine of Table 3 and/or in the Iron Precipitation Discharge Liquor (2) of Figure 20.

330. “Subsequent precipitation of manganese, lead, and zinc would thus provide a solid product much lower in iron and of greater commercial value than that produced by the process given in the preceding section.” *Id.*, at 20.

331. *Christopher* discloses removing zinc from the substantially silica free brine.

332. Similar to silica and iron removal, zinc is precipitated from the geothermal brine by using air and lime. In Table 3, the zinc amount is seen to have been reduced from 0.497 g/L (421.5 mg/kg³) in the Feed Brine to 0.004 g/L (3.4 mg/kg) in the Product Brine. *Id.*, at 12.

333. Similarly, in Figure 20, the zinc concentration of 805 ppm in the Feed Brine (1) is reduced to 780 ppm in the Iron Precipitation Discharge Liquor (2) further reduced to 5.0 ppm in the Manganese Precipitation Discharge Liquor (3), and still further reduced to less than 1 ppm in the Product Brine (4). The precipitated zinc solids that are removed from the Iron Precipitation Discharge Liquor (2) are filtered and washed to produce a Mixed Oxide Product (6). *Id.*, at 42.

334. Like *Christopher*, the embodiments of Figures 1 and 4-11 and Examples 4-5 of the ‘117 patent precipitate zinc from the synthetic brine by oxidizing with air the

³ mg/kg=(g/L*1000)/1.18kg/L due to the density of Salton Sea geothermal brines.

ferrous iron to ferric iron and controlling the pH with the addition of a lime slurry added to control the pH of the brine.

335. *Christopher* discloses extracting manganese from the substantially silica free brine.

336. Similar to zinc removal, manganese is precipitated from the geothermal brine by using air and lime. In Table 3, the manganese amount is seen to have been reduced from 1.63 g/L (1,381 mg/kg) in the Feed Brine to 0.002 g/L (1.69 mg/kg) in the Product Brine. *Id.*, at 12.

337. Similarly, in Figure 20, the manganese concentration of 2000 ppm in the Feed Brine (1) remains constant at 2000 ppm in the Iron Precipitation Discharge Liquor (2), which is then reduced to less than 1 ppm in the Manganese Precipitation Discharge Liquor (3) and the Product Brine (4). The precipitated manganese solids that are removed from the Iron Precipitation Discharge Liquor (2) are filtered and washed to produce a Mixed Oxide Product (6). *Id.*, at 42.

338. Just like *Christopher*, the embodiments of Figures 1 and 4-11 and Examples 4-5 of the '117 patent extract manganese from the synthetic brine by oxidizing with air the ferrous iron to ferric iron and controlling the pH with the addition of a lime slurry was added to control the pH of the brine.

339. *Featherstone I* was admitted as prior art in the specification of the '117 patent, and *Featherstone I* teaches the need to clarify the brine before zinc removal (EX

1011, 3:41-42) after which the clarified brine is passed over an ion exchange resin that binds zinc. *Id.*, 2:14-15; 4:18-19.

340. Iron and other contaminating metals are removed from the zinc-rich eluate by oxidation, after which zinc is removed using a solvent extraction process with an organic solvent. *Id.*, 6:56-59; 7:25-31.

341. Iron and other contaminating metals are removed from the zinc-rich eluate by oxidation, after which zinc is removed using a solvent extraction process with an organic solvent, such as di-2-ethyl-hexyl phosphoric acid (D2EHPA). *Id.*, 2:19-24; 6:56-59; 7:25-31. This is the same organic solvent disclosed by the ‘117 patent. (“The solvents can include, for example, water-immiscible cationic organic solvents, such as di-2-ethyl-hexyl phosphoric acid (D2EHPA), or other similar solvents, as known in the art.” EX 1001, 11:10-13.).

342. *Featherstone II* is from the same field of art as the ‘117 patent, and clearly discloses oxidizing manganese that has been extracted from a brine to produce manganese dioxide at the anode of an electrolysis cell. EX 1012, [0084].

343. *Featherstone II* was admitted as prior art in the specification of the ‘117 patent, and discloses a “process for producing electrolytic manganese dioxide from geothermal brines”. EX 1012, Title. Manganese and iron are extracted from the geothermal brine solution using solvent extraction, and then stripped with an acid.

344. *Featherstone II* discloses diethyl-hexylphosphate (DEPHA or D2EPHA) and Cyanex 272 as exemplary organic solvents for the extraction of manganese. *Id.*, [0057].

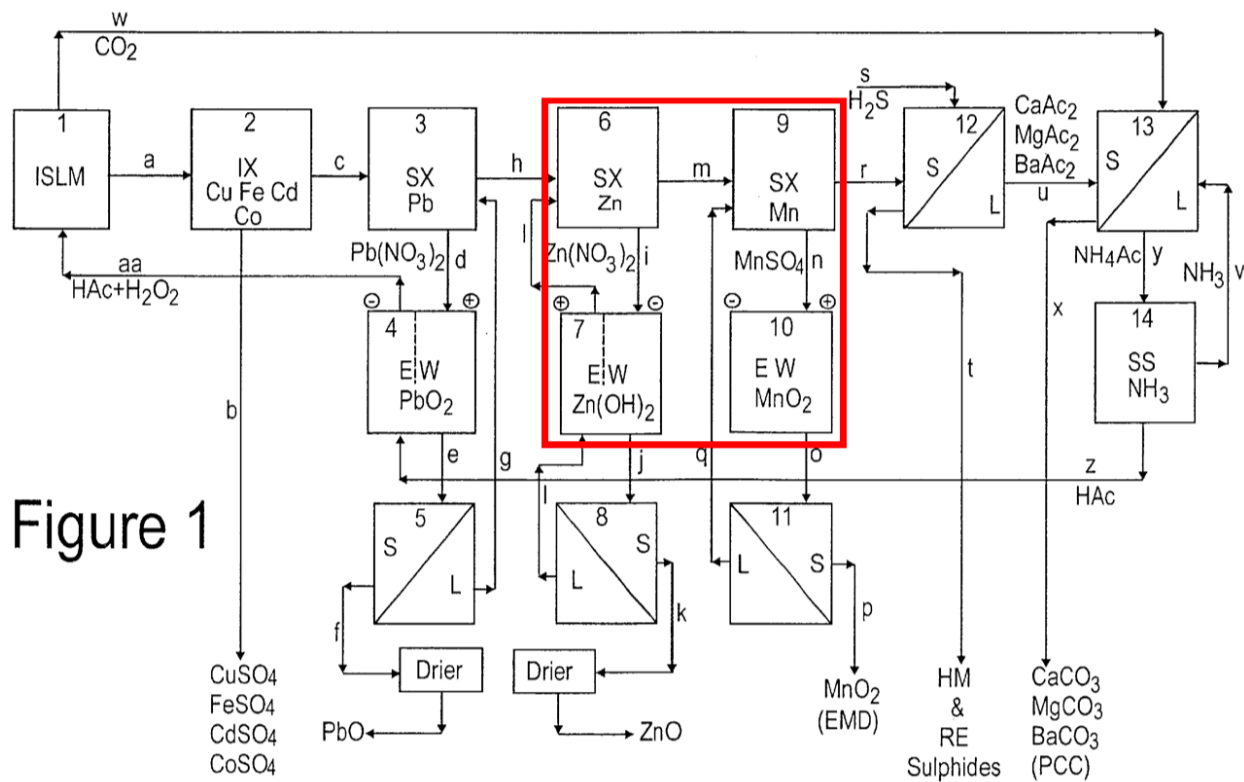
345. The iron is then oxidized, and iron precipitates leaving a supernatant containing manganese. The supernatant containing manganese is then oxidized in an electrowinning cell such that electrolytic manganese dioxide is precipitated therefrom onto the anode of the electrolysis cell. *Id.*, [0022].

346. During electrowinning, manganese dioxide is deposited in the form of a dense precipitate layer at the anode. *Id.*, [0084]. “The final manganese produce is preferably comprised of at least 99% pure manganese dioxide.” *Id.* [0088].

347. *Featherstone II* discloses that “[f]ollowing the electrowinning step, the manganese dioxide product deposited on the anode is optionally finished to produce a commercial product. ... The manganese dioxide may then be removed using mechanical forces such as agitation, flexing, scraping, etc. Finally, the manganese dioxide may be ground, milled and neutralized using known methods.” *Id.*, [0086].

348. *Geisler* discloses “Lead, Zinc and Manganese Recovery from Aqueous Solutions.” EX 1009, at Title. *Geisler* initially removes iron and other interfering metals from aqueous solutions or leachates using ion exchange, and then preferentially extracts lead, then zinc and then manganese in that order using solvent extraction followed by electrowinning. *Id.*, at Abstract. *Geisler’s* aqueous solution

or leachate is a “brine” as that term is defined in the ‘117 patent. Figure 1 of *Geisler* is reproduced below:



Id., highlighting added.

349. *Geisler* teaches removing zinc from a substantially silica and iron-free brine using solvent extraction (Block 6) intermediate of iron impurity removal (Block 2) and manganese extraction (Blocks 9, 10 and 11). *Id.*

350. Block 9 of *Geisler* teaches preferentially extracting manganese after lead and zinc using solvent extraction (Block 6). Manganese extraction (Blocks 9, 10 and 11) is conducted after iron impurity removal (Block 2). *Id.*

351. *Brown* discloses “Method of Extracting Zinc from Brines” (EX 1010, Title), “as well as a number of other elements including manganese, iron, lead, silver, magnesium, strontium and lithium.” *Id.*, 2:30-35. “After substantially all silica is removed,” the brine is then run through the circuit shown in Figure 1. *Id.*, 2:46-49.

352. *Brown* recognizes “[t]he silica solids which have precipitated in the brines as a result of cooling and loss of acid gases are desirably removed from the brines prior to the solvent extraction process. Their removal can be achieved through careful and efficient liquid-solid separation techniques.” *Id.*, 3:54-59.

353. *Brown* goes on to disclose removing “substantially all silica” from a geothermal brine before contacting the brine with an organic solvent that extracts zinc, iron and manganese therefrom. *Id.*, 3:50-68; 4:10-13.

354. *Brown* describes providing the treated geothermal brine with zinc, manganese and other elements to a continuous solvent extraction circuit for sequential zinc and manganese recovery from the geothermal brine. *Id.*, 3:15-21; 4:15-18.

355. *Maimoni, Bourcier, Christopher, Featherstone I, Featherstone II, Geisler and Brown* are each from the same field of endeavor as the ‘117 patent, namely recovering zinc and manganese from geothermal brines and aqueous solutions.

356. Since a POSITA would not only look to known solutions for geothermal brines, a POSITA who sought to solve the problem set out in the ‘117 patent would

also look to the teachings of other brine processing, hydrometallurgy or ore recovery operations for readily adaptable solutions.

357. As such, a POSITA who sought to solve the problem set out in the ‘117 patent would find these references of particular relevance because they all detail methods of recovering zinc, manganese and other minerals and metals from geothermal brines and aqueous solutions.

358. In addition, *Jost* and *Wilkins* deal with processing Salton Sea geothermal brines, and teach selective removal of silica and iron from geothermal brines.

359. *Jost* discloses selective removal of silica and iron from “silica-rich geothermal brines, representative of which are those found in the Imperial Valley of Southern California.” EX 1007, Abstract; 2:26-28.

360. *Jost* teaches a process for stabilizing silica-rich geothermal brine to prevent silica scaling. *Id.*, Abstract. The process taught by *Jost* includes:

selectively providing a supply of ferric ions, allowing the silica-rich brine to combine with the ferric ions to form insoluble, iron-rich siliceous material and separating the insoluble siliceous material from the brine to form a brine having a silica content which is reduced below the saturation level required for substantially scale-free handling of the brine. In one embodiment of the process in which the brine contains sufficient dissolved ferrous ions, the process comprises selectively contacting the brine with an oxidizing agent, preferably by aerating the brine, to oxidize a selected portion of the ferrous ions to ferric ions, which then combine with silica to form the insoluble iron-rich siliceous material.

Id.

361. “[T]he process is effective for removing silica from silica-rich geothermal brine so as to provide substantially silica scale-free brine reinjection, or other disposal or use.” *Id.*, 3:16-20, emphasis added. Accordingly, *Jost* removes or reduces silica and iron from the geothermal brine to produce a “substantially silica free brine” as that term is used in the ‘117 patent.

362. *Wilkins* is directed at a process for the removal of silica from geothermal brine. EX 1008, Title.

363. *Wilkins* discloses using air to oxidize ferrous hydroxide to ferric hydroxide, which form a precipitate that is less likely to stick on equipment surfaces. *Id.*, 5:45-50. The precipitate is removed from the bottom of a settling tank, the liquid fraction is filtered, and the filtrate is discharged to a disposal line for injection into a disposal well. *Id.*, 6:12-20.

364. Based on the pH and oxidizing conditions of *Wilkins*, a substantially silica free brine is produced that includes zinc and manganese.

365. As noted above, *Maimoni*, *Bourcier*, *Christopher*, *Featherstone I*, *Featherstone II*, *Geisler* and *Brown* are each from the same field of endeavor as the ‘117 patent, namely recovering zinc and manganese from geothermal brines and aqueous solutions. In addition, *Jost* and *Wilkins* deal with processing Salton Sea geothermal brines, and teach selective removal of silica and iron from geothermal brines to produce substantially silica free brines.

366. In each case, the prior art references are each directed at the recovery of minerals from geothermal brines produced from the Imperial Valley in California, and it would have been obvious to a POSITA to refer to the teachings of these references at the time of the invention of the '117 patent since each reference, taken individually, teaches this claim limitation.

367. To the extent that *Maimoni*, *Bourcier*, and *Christopher* are interpreted to not disclose selectively removing silica and iron, given the similarities in the subject matter and teachings from *Maimoni*, *Bourcier*, *Christopher*, *Brown*, *Jost* and *Wilkins*, it would have been obvious for a POSITA to combine teachings from one reference with teachings from another to the extent that the individual references do not disclose this limitation.

368. A POSITA would have been motivated to combine *Maimoni* and/or *Brown* and/or *Jost* and/or *Wilkins* with *Bourcier* and/or *Christopher* to reduce silica and iron concentrations in geothermal brines in order to improve mineral extraction and recovery.

369. A POSITA confronted with the problem of recovering minerals (e.g., zinc and manganese) from geothermal brines would understand that silica removal prior to mineral recovery may be achieved by modifying the processes of *Maimoni* and/or *Bourcier* and/or *Christopher* to selectively remove silica and iron from the geothermal brine as in *Brown* and/or *Jost* and/or *Wilkins*.

370. The processes of *Maimoni, Brown, Jost* and/or *Wilkins* selectively remove silica and iron, and leave manganese and zinc for subsequent mineral recovery, such as by the method of *Maimoni, Bourcier, Christopher, Featherstone I, Featherstone II, Brown* and/or *Geisler*.

371. This merely substitutes the silica and iron removal steps of *Bourcier* and/or *Christopher* with that of *Maimoni, Featherstone I, Featherstone II, Brown, Jost* and/or *Wilkins* to yield predictable results.

372. In my opinion, a POSITA who was seeking to solve the problem of the '117 patent and who had knowledge of *Maimoni, Bourcier, Christopher, Featherstone I, Featherstone II, Brown, Geisler, Jost* and/or *Wilkins* would recognize that the silica free brine of *Maimoni, Brown, Jost* and/or *Wilkins* could be used as input to the zinc and/or manganese removal steps of *Maimoni, Bourcier, Featherstone I, Featherstone II, Christopher, Brown* and/or *Geisler*.

373. Moreover, a POSITA would recognize that manganese could be removed by precipitation by following the teachings of *Maimoni* and/or *Christopher* or could be removed by solvent extraction and ion exchange by following the teachings of *Bourcier, Featherstone I, Featherstone II, Brown* and/or *Geisler*. This merely substitutes the zinc removal and/or manganese extraction steps of *Maimoni* and/or *Christopher* with that of *Bourcier, Featherstone I, Featherstone II, Brown* and/or *Geisler* to yield predictable results.

374. Yet further, it would have been obvious to combine *Maimoni* and/or *Christopher* with *Geisler* and/or *Featherstone II* in order to oxidize the manganese to produce a manganese dioxide precipitate and then recover the manganese dioxide precipitate using typical methods, namely filtration.

375. With a clarified brine from *Maimoni*, *Brown*, *Jost* and/or *Wilkins* from which zinc has been removed and manganese has been extracted, such as by the method of *Maimoni*, *Bourcier*, *Christopher*, *Featherstone I*, *Featherstone II*, *Brown* and/or *Geisler*, manganese dioxide precipitate could be produced by electrochemical oxidation at the anode of an electrochemical cell, and then recovered using the method of *Featherstone II* and/or *Geisler*.

IX. CONCLUSION

376. The findings and opinions set forth in this declaration are based on my work and examinations to date. I may continue my examinations. I may also receive additional documentation and other factual evidence over the course of this proceeding that will allow me to supplement and/or refine my opinions. I reserve the right to add to, alter, or delete my opinions and my declaration upon discovery of any such additional information. I reserve the right to make such changes as may be deemed necessary.

377. In signing this declaration, I recognize that the declaration will be filed as evidence in a contested case before the Patent Trial and Appeal Board of the United

States Patent and Trademark Office. I also recognize that I may be subject to cross-examination in the case and that cross-examination will take place within the United States. If cross-examination is required of me, I will appear for cross-examination within the United States during the time allotted for cross-examination.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information are believed to be true. I understand that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code.

Respectfully submitted,

Dated: September 30, 2019

Darrell L. Gallup, Ph.D.
Darrell L. Gallup, Ph.D.

EXHIBIT A

Darrell L. Gallup, Ph.D.



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Solving Process Chemistry and Engineering Problems

41 years experience in Production Optimization for the Petroleum Industry. Internationally recognized authority on oil / gas production, chemistry, flow assurance, geothermal energy production, water treatment and environmental processes. "Hands on" problem solving and process development philosophy (Laboratory → Pilot →

Demonstration → Commercialization) has delivered an impressive track record of success in solving complex process chemistry and engineering problems.

Examples of accomplishments:

Industry/Area

1. Geothermal silica scaling
2. Mercury removal from crude oil
3. Water treatment
4. Water treatment
5. Mineral recovery
6. Soap emulsions
7. Hydrogen sulfide abatement
8. Water treatment
9. Corrosion control
10. Mercury partitioning

Solution

1. Developed pH modification scale control technology into a commercial process. Scale inhibition in steam floods, SAGD.
2. Assisted in development and pilot testing of process that is installed commercially at oilfield in Argentina. Operating successfully for 12 years. New installation pending.
3. Developed improved process to remove mercury and arsenic from oilfield produced water. Operating for 15 years.
4. Developed copper precipitation process to remove selenium from refinery wastewater. Operating commercially for 20 years.
5. Developed processes used commercially to recover silver from geothermal brines.
6. Identified new type of emulsion and applied new inhibitors in Indonesia to prevent formation. Allows crude sales.
7. Developed new process installed in 2 Salton Sea geothermal cooling towers.
8. Implemented lowest cost geothermal cooling tower treatment in Indonesia.
9. Assisted in developing acid corrosion control at Geysers geothermal field. Dry steam scrubbing process at Geysers.
10. Model predicts distribution in oil and gas operations.

Professional Experience	9 years Thermochem, Inc., Santa Rosa, CA. Sr. Process Chemist		
	5 years Chevron Energy Technology Co., Houston, TX. Sr. Consultant		
	25 years Unocal Corporation; Science & Technology Div., Brea, CA; Corporate Environmental Remediation Technology, Brea, CA; Geothermal & Power Operations, Santa Rosa, CA		
	2 years Texaco Exploration & Production Research, Bellaire, TX		
Education	1974 – 1978	Utah State University	Logan, UT
	<ul style="list-style-type: none"> • Ph.D. Inorganic Chemistry 		
	1972 – 1974	Brigham Young University	Provo, UT
	<ul style="list-style-type: none"> • B.S. Chemistry • NSF Undergraduate Research Fellow University of Idaho 		
Miscellaneous	<p>Inventor of 62 US patents and numerous foreign counterparts. 1 US patent pending. Published 94 technical papers and 5 book chapters. <u>SPE Production Engineering</u> Editorial Board - current member. <u>Geothermics</u> Editorial Board, 2000-2006. <u>Geothermics</u> Advisory Board, 2007- present. Chairman, NACE Geothermal Committee, 1999–2005; Vice-chairman 2011-2015. Chairman IQPC Europe 2003 Produced Water Management Conference. Chairman IQPC SE Asia 2008 Produced Water Conference. Chairman pro-tem 33rd IGC geothermal session. SPE 2009 Scale Workshop committee. Provider of training class - mercury management in the petroleum industry.</p>		
Awards	2012 Pioneer Award – Geothermal Resources Council; 1998 Hugh Tokley Award – New Zealand geothermal workshop.		
Memberships	American Chemical Society, International Geothermal Association/Geothermal Resources Council, National Association of Corrosion Engineers, Society of Petroleum Engineers.		
Consulting Clientele	<p>Advanced Sensors; Apache Corp., Arsenic Solutions; California Energy; Cameron; Chevron Geothermal; Chevron USA; CobiaGeo; ConocoPhillips; CRAAsia; Cyrq Energy; Dansk Geotermi; Dipa Geothermal; EnergySource; Exterran; GeoPark; GERD-Japan; Greymouth Petroleum; INPEX, Khalda Petroleum; Lawrence Berkeley Laboratory; Mighty River Power; MontgomeryWatsonHartz; Origin Energy; Petronas; Polaris Geothermal; Portnoy Environmental; Puna Geothermal; Ram Power; Santos; Simbol Materials; Statoil; The Shaw Group; Tuzla Geothermal; US Geothermal; Valero Refining; Westinghouse Savannah River; Wood Group; WorleyParsons,</p>		
Experience/Skills	Mentoring of foreign nationals, training courses, expert witness, patents & licensing.		

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PRESENTATIONS

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