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 FROM GEOTHERMAL BRINES

IPR2019-01605

PETITION FOR *INTER PARTES* REVIEW OF U.S. PATENT NO. 9,057,117

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1001	U.S. Patent No. 9,057,117 ("the '117 patent"; EX 1001)
1002	Prosecution History of the '117 patent
1002	Declaration of Dornall L. Callun, Dh. D.
1003	Declaration of Darrell L. Gallup, Ph.D.
1004	Maimoni, A., A Cementation Process for Minerals Recovery from
	Salton Sea Geothermal Brines, Lawrence Livermore Laboratory,
	January 26, 1982 ("Maimoni"; EX 1004)
1005	Bourcier, et al., Recovery of Minerals and Metals from Geothermal
	<i>Fluids</i> , 2003 SME Meeting, Feb. 24 – Feb. 26, 2003 (" <i>Bourcier</i> "; EX
1000	$\frac{1005}{1005}$
1006	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 (" <i>Christopher</i> "; EX 1006)
1007	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)
1008	U.S. Patent No. 4,016,075, for "Process for Removal of Silica From
	Geothermal Brine", to Wilkins, <i>et al.</i> , filed March 17, 1975, and issued
1000	April 5, 1977 (" <i>Wilkins</i> "; EX 1008)
1009	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 (" <i>Geisler</i> "; EX 1009)
1010	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)
1011	U.S. Patent No. 6,458,184, for "Recovery of Zinc from Geothermal
	Brines", to Featherstone, filed December 20, 2000, and issued October
1010	1, 2002 ("Featherstone I"; EX 1011)
1012	U.S. Patent Publication No. 2003/0226761, for "Process for Producing
	Electrolytic Manganese Dioxide from Geothermal Brines", to Featherstone, <i>et al.</i> , filed May 31, 2002, and published December 11,
	2003 (<i>"Featherstone II"</i> ; EX 1012)

1013	Declaration of Wayne Strickland-NTIS-Maimoni
1014	Declaration of Wayne Strickland-NTIS-Bourcier
1015	Declaration of Deborah Cutler-OSTI-Maimoni
1016	Declaration of Deborah Cutler-OSTI - Bourcier

I. <u>INTRODUCTION</u>

Petitioner EnergySource Minerals, LLC ("Petitioner") requests *Inter Partes* Review ("IPR") of Claims 12-15 and 20 (the "Challenged Claims") of U.S. Patent No. 9,057,117 (the '117 patent). This Petition demonstrates there is a reasonable likelihood that Petitioner will prevail in proving, by at least a preponderance of the evidence, that the Challenged Claims are unpatentable over prior art that the U.S. Patent and Trademark Office ("USPTO") did not have or did not fully consider during prosecution. For the reasons addressed below, the Challenged Claims should be found unpatentable and canceled.

II. <u>MANDATORY NOTICES</u>

a. Real Party-in-Interest

The real party-in-interest is EnergySource Minerals, LLC, a Delaware limited liability company. No unnamed entity is funding, controlling, or directing, or otherwise has an opportunity to control or direct this Petition or proceeding.

b. Related Matters

Petitioner is concurrently filing IPR petitions on U.S. Patent Nos. 8,518,232 and 9,238,851, along with 8,454,816 which is the continuation parent patent of the '117 patent.

c. Lead and Back-up Counsel

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d. Service Information

Service information for lead and back-up counsel is provided above in the designation of lead and back-up counsel. Petitioner also consents to electronic service by email at <u>ESM.IPR@crowedunlevy.com</u>.

III. <u>PAYMENT OF FEES</u>

Payment for the fees set forth in 37 C.F.R. § 42.15(a)(1-2) accompanies this Petition. Petitioner also authorizes the USPTO to charge Deposit Account No. 13-0110 for any additional fees that may be due for this Petition.

IV. <u>REQUIREMENTS FOR IPR</u>

a. Grounds for Standing

Petitioner certifies that the '117 patent is available for IPR and that Petitioner is not barred or estopped from requesting IPR of the Challenged Claims on the grounds identified herein.

b. Identification of Challenge

Petitioner requests cancellation of the Challenged Claims in the '117 patent as unpatentable over the prior art for the following grounds:

1. **Ground 1:** Claims 12-15 and 21 are anticipated by *Miamoni* (EX 1004) and/or obvious over *Miamoni* (EX 1004) in view of Applicant Admitted Prior Art ("AAPA") and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).

2. **Ground 2:** Claims 12, 14-15 and 21 are anticipated by *Bourcier* (EX 1005) and/or obvious over *Bourcier* (EX 1005) in view of AAPA and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).

3. **Ground 3:** Claims 12-15 and 21 are anticipated by *Christopher* (EX 1006) and/or obvious over *Christopher* (EX 1006) in view of AAPA and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).

4. **Ground 4.** Claims 12-15 and 21 are obvious over *Maimoni* (EX 1004) and/or *Bourcier* (EX 1005) and/or *Christopher* (EX 1006) in view of *Jost* (EX 1007) and/or *Wilkins* (EX 1008) and/or *Brown* (EX 1010), and in further view of *Geisler* (EX 1009) and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).

V. LEVEL OF SKILL IN THE ART

The level of skill in the art is apparent from the cited art. Further, a person of ordinary skill in the art ("POSITA") 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 experience, and an understanding of the relevant principles of chemistry and chemical engineering and hydrometallurgy technology. EX 1003, ¶22.

VI. <u>SUMMARY OF THE '117 PATENT</u>

a. Priority Date

The '117 patent was filed as Application No. 13/874,004 on April 30, 2013, and the earliest possible effective U.S. filing date for the '117 patent is September 11, 2009. While Petitioner does not accede to an invention or priority date of September 11, 2009 for the '117 patent, for purposes of this Petition only it is assumed that all of the claims of the '117 patent are entitled to that date. Accordingly, any art published before April 30, 2013 is prior art under 35 U.S.C. §102(a)¹, any art published before September 11, 2009 is prior art under 35 U.S.C. §102(b), and patents granted on applications filed before April 30, 2013 are prior art under §102(e).

b. Description of the Alleged Invention of the '117 Patent

The '117 patent relates to a method for the selective recovery of manganese and zinc from geothermal brines. It includes the steps of removing silica and iron from the brine, oxidizing the manganese and zinc to form precipitates, 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.

The '117 patent acknowledges that silica coprecipitates with other metal species in geothermal brines, and that removal of silica helps reduce scaling and fouling of the injection wells and processing equipment. *Id.*, at 1:31-57. The '117 patent goes on to allege that "[a]lthough conventional processing of ores and brines currently employed can be used to recover a portion of the manganese and zinc present in geothermal brines, there still exists a need to develop economic methods

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 are selective for the removal and recovery of manganese and zinc from the brines at high yields and high purity." *Id.*, 1:52-57.

c. Summary of the Prosecution History of the '117 Patent

The '117 patent was filed April 30, 2013. EX 1002.

A preliminary amendment was filed concurrently with the application to amend the claims "for the purpose of filing a continuation application". As-filed Claims 1-20 were canceled, and new Claims 21-41 introduced. *Id.*, at 132-138.

In an Office Action dated December 29, 2014, Claims 21-41 were provisionally rejected based on nonstatutory double patenting in view of the parent patent, U.S. Patent Nos. 8,518,232 and 8,454,816 and co-pending U.S. Patent Application No. 13/943,395 (now U.S. Patent 9,238,851). *Id.*, at 76-82.

The Examiner's Notice of References Cited listed only two patents, both of which were owned by the applicant: U.S. Patent No. 8,454,816 and the parent patent U.S. Patent No. 8,518,232. *Id*, at 83.

A response to the Office Action was submitted that contained terminal disclaimers. *Id.*, at 55-74.

A Notice of Allowance was issued April 15, 2015, allowing all pending claims without substantive discussion. *Id.*, at 23-29. In the Notice of Allowance, the Examiner stated the reasons for allowance were that "It is proper when the only rejection outstanding is an obvious type double patenting, to allow the first

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application while requiring the filing of the terminal disclaimer for the second application. Accordingly, the claims are allowable." *Id.*, at 36.

Claims 21-41, which were added on April 30, 2013, matured into issued Claims 1-21 of the '851 patent.

VII. <u>CLAIM CONSTRUCTION</u>

The claims of the '117 patent should be construed under the *Phillips* standard.

37 C.F.R. § 42.100(b); see generally Phillips v. AWH Corp., 415 F.3d 1303 (Fed.

Cir. 2005) (en banc).

a. "brine"

The '117 patent defines the term "brine" 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, 5:54-60, emphasis added. Petitioner proposes that the term "brine" should

be defined as indicated above. EX 1003, ¶44.

b. "selectively removing silica and iron"

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.

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.

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; Figures 1-11.

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.

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.

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.

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Id., 6:59-63, emphasis added. The '117 patent further acknowledges that "depending upon the pH of the solution, a lead precipitate may also be formed." *Id.*, 7:28-30.

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. EX 1003, ¶52.

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. EX 1003, ¶53.

c. "substantially silica free brine"

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.

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 ...

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. ... 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.

EX 1001, 6:22-24; 7:3-13, emphasis added.

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.

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. EX 1003, ¶57.

Accordingly, Petitioner proposes 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. *Id.*, ¶58.

d. "removing the zinc"

Claims 12 and 21 include the phrase "removing the zinc", which is not defined in the '117 patent.

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





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

•••

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., 7:19-43, emphasis added.

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; Examples 4-5.

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.

The '117 patent provides that "[t]he 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....., such as is described in U.S. Pat. No. 6,458,184 [*Featherstone I* EX 1011], which is incorporated 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.

In Figure 3, "manganese and zinc can be **removed** by liquid-liquid extraction step 320" (*i.e.*, solvent extraction). *Id.*, 11:4-6.



Id., at Figure 3, highlighting added.

"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.

As such, Petitioner submits that the phrase "removing the zinc" in the context of Claims 12 and 21 should be construed as removing or separating zinc from the brine by precipitation, solvent extraction or ion exchange. *Id.*, ¶¶66, 69, 73-74.

e. "extracting manganese"

Claims 12 and 21 include the phrase "extracting manganese"; however, this phrase is not defined in the '117 patent.

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





"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.

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 4-10; Examples 4-5.

In addition, Step 230 indicates that manganese are 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.

Similar to the zinc removal step discussed above, in 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 D2EHPA, "and other similar solvents, as known in the art." *Id.*, 11:12-13.

Therefore, Petitioner submits that for purposes of construction of this phrase as used in the '117 patent, the phrase "extracting manganese" should be construed as extracting or separating manganese from the brine by precipitation, solvent extraction or ion exchange. *Id.*, ¶¶82, 84, 87-88.

f. "oxidizing the manganese"

Claim 12 includes the phrase "oxidizing the manganese", but that phrase is not defined in the '117 patent.

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.

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.

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.*

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.

"[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. "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.

Petitioner submits that "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. EX 1003, ¶¶93, 97-98.

g. "recovering the manganese dioxide precipitate"

Claim 12 of the '117 patent includes the phase

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. EX 1001, 9:4-7; 10:51-52; 12:46-49; 13:15-17, emphasis added; Figures 1-2, 4-6.

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. EX 1003, ¶101.

h. "providing iron (III)"

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.

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. EX 1003, ¶103.

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. EX 1003, ¶104.

VIII. <u>UNPATENTABILITY OF THE CONSTRUED CLAIMS</u>

a. Summary of the Prior Art

The prior art relied upon relates to the fundamental object of the Challenged Claims, *i.e.*, to limit iron silicate scaling caused by the processing of geothermal brines and to remove the resulting precipitated iron-silica complexes, with the resulting clarified brine being processed for mineral recovery. Each prior art reference is from the same field of endeavor as that of the '117 patent, *i.e.*, the processing of geothermal brines for the production of power and/or the recovery of minerals. EX 1003, ¶365. Moreover, a POSITA who was seeking to solve the

problem set out in the '117 patent would find the prior art cited to be especially relevant. *Id.*, ¶366.

1. *Maimoni* (EX 1004)

Maimoni provides an overview of the then-current efforts to recover minerals from Salton Sea geothermal brines. EX 1004, at 1. *Maimoni* describes the processes utilized by Hazen Research Incorporated ("Hazen") at a pilot plant operated at the Magmamax No. 1 well in the Salton Sea. *Id.*, at 14. *Maimoni* notes that the Hazen process "is based on selective precipitation of the hydroxides using lime. They found better separation when the iron was oxidized to the ferric state by sparging air through the brine." *Id. Maimoni* explains that Hazen's "experiments also indicated that it would be advantageous to remove the silica present in the brine before precipitating the heavy metal hydroxides." *Id.*

Table 5 and Figure 5 in *Maimoni* show the complete design flow sheet and compositions of Hazen's 15-gpm pilot plant:



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

					S	Strea	m No.					
	1	2	3	4	5	6	7	8	9	10	11	12
SiO2	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/g
NH3	352 ppm			352 ppm				352 ppm			352 ppm	
Post.	Internet Sources	Solution color	07.30°	sor tool	ANT JULT RES	LO BE CO	or House	und to the state	North States I took	HO OF	A CALLON CALL	ANY SURA

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

						5	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
Рь			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
NH3		3.0 lb/h	352 ppm			35 ppm			35 ppm			35 ppm
VIII STORE	Carlon Carlos	Introl North	Tickeret Margines	Collog Hori	See 30 And	Non	Not AND AND	Super	tridere surrive	Creation Little Little	un an	in so non

Id., at 15-17.

2. Bourcier (EX 1005)

Bourcier summarizes mineral and metal extraction projects from various geothermal brine sources, including a Salton Sea geothermal brine. EX 1005, Title and Abstract. Bourcier "discusses the opportunities, the processes, the challenges, the current status, the economics and the potential for recovery of minerals and metals from geothermal fluids." Id., at Abstract. Bourcier notes that silica which is a "ubiquitous component" of geothermal brines must be removed or reduced in concentration before other components of the brine can be removed. Id., at 6. Bourcier also recognized that the disclosed process for removing silica will also precipitate iron. Id., at 12. Bourcier describes a case history of CalEnergy Minerals zinc and manganese extraction plant at the Salton Sea in the Imperial Valley of southern California. Id., at 11-13. Bourcier reports that CalEnergy removed zinc using ion exchange and solvent extraction from "spent brine" downstream of its geothermal power production facility. *Bourcier* further reports that "CalEnergy has investigated methods for extracting manganese from their brines", with the target producing being electrolytic manganese dioxide. Id., at 13. Bourcier notes that solvent extraction using phosphoric acid and an amine showed good selectively for manganese. Id.

3. Christopher (EX 1006)

Entitled "*The Recovery and Separation of Mineral Values from Geothermal Brines*," this 1975 publication provides a description of the then-current efforts to recover and separate minerals from geothermal brines from the Sinclair No. 4 well in Imperial Valley, California. EX 1006, at 7. *Christopher* summarizes the work done and results obtained by Hazen for the recovery of iron, manganese, zinc, lithium, and other minerals and metals from Salton Sea geothermal brines. *Id*.

Figure 20 of *Christopher* discloses a batch process for impurity removal followed by mineral extraction:



FLOWSHEET FOR BRINE PURIFICATION

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

	Wt.	CONCENTRATION, %						
SOLID	g. '	Min	Fe	Zn	Рb	Li		
5 IRON OXIDE Product	4.9	< 0.1	68.0	0.9	0.4			
6 MIXED OXIDE	8.5	47.3	0. 6	18.2	2 <i>.</i> 8	-		
TITHIUM ALUMINUM	· –	-	-	-	-	3.7		

FIGURE 20 hri

Id., at 42.
4. *Jost* (EX 1007)

Jost describes a process for stabilizing silica-rich geothermal brine to prevent silica scaling. EX 1007, Abstract. Jost includes the steps of selectively providing a supply of ferric (iron III) 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. *Id.* In one embodiment 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.*

5. Wilkins (EX 1008)

Wilkins discloses in Figure 2 selectively precipitating silica and iron to produce a clarified geothermal brine wherein the dissolved silica in the brine is reduced by more than 90% relative to the feed brine.



EX 1009, Figure 2, highlighting added.

Wilkins is also directed at a process for the removal of silica from geothermal brine. EX 1008, Title. *Wilkins* discloses using air to oxidize ferrous hydroxide to ferric hydroxide, which is then injected into the reaction chamber. *Id.*, 5:45-50. *Wilkins* discloses that ferric hydroxide and ferrous hydroxide form a mixture that makes the sludge less gelatinous and therefore less likely to stick on equipment surfaces. *Id.* 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.

6. *Geisler* (EX 1009)

Geisler concerns recovery of lead, zinc and manganese from aqueous solutions or leachate by sequential solvent extraction. EX 1009, Abstract. *Geisler* is from the same field of endeavor as that of the '117 patent as it deals with aqueous solutions or leachate from, for example, mining that contain concentrations of lead, zinc, and manganese plus other alkaline earth metals in solution. *Id.*, 4:23-28. *Geisler's* leachate is a "brine" as that term is used in the '117 patent. EX 1003, ¶197.

Figure 1 of *Geisler* is reproduced below:



Geisler preferentially and sequentially extracts manganese using solvent extraction followed by electrowinning after removing any interfering minerals and metals. EX 1009, Figure 1.

7. Brown (EX 1010)

Brown describes an improved method of extracting zinc selectively from a geothermal or synthetic brine which may contain other metal ions, including, without limitation, manganese, iron, lead, silver, magnesium, manganese, strontium, calcium, sodium, potassium and lithium. EX 1010, 3:16-21. *Brown* describes a process in which substantially all of the insoluble, amorphous silica is removed from the brine before the zinc and other metal ions are removed. *Id.* 3:50-68.

8. Featherstone I (EX 1011)

Featherstone I 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.

9. Featherstone II (EX 1012)

Featherstone II discloses a "process for producing electrolytic manganese dioxide from geothermal brine" (EX 1012, Title), and more particular "a liquid-liquid extraction method for separating manganese dioxide from brine using an electrolytic process." *Id*, [0001].

b. Introductory Arguments

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, extract manganese from the clarified brine and then further refine the extracted manganese to electrolytic manganese dioxide.

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.

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) and/or *Featherstone I* (ion exchange and solvent extraction) and/or *Featherstone II* (solvent extraction). Further, the extracted manganese could be further process to produce manganese dioxide and/or *Featherstone II*.

c. Ground 1: Claims 12-15 and 21 are anticipated by and/or obvious over *Maimoni* (EX 1004) in view of AAPA and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).

1. Claims 12 and 21

For brevity, the common limitations of Claims 1 and 10 are addressed together below.

i. A method for recovering zinc and manganese from a brine, the method comprising the steps of (Claims 12 and 21)²:

² For purposes of the instant proceeding only, Petitioner will assume that the preamble of the Challenged Claims actually function as a claim limitation. However, Petitioner reserves the right in future proceedings to challenge whether or not this preamble "breathes life and meaning into the claim". *In re Wertheim*, 541 F.2d 257 (CCPA 1976).

Maimoni is directed to "A Cementation Process for Minerals Recovery from Salton Sea Geothermal Brines". EX 1004, Title. 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.

ii. providing a brine, said brine comprising manganese and zinc (Claims 12 and 21);

Stream 1 of Table 5 of *Maimoni* provides the Magmamax No. 1 geothermal brine having manganese and zinc to a silica reactor:

	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			
NH3	352 ppm			

Id., at 16, highlighting added.

iii. selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc (Claims 12 and 21);

Maimoni selectively precipitates silica and metal hydroxides from Magmamax No. 1 geothermal brine using lime. *Id.*, at 14. In particular, *Maimoni* selectively removes silica from the brine between Streams 1 and 4, and further selectively removes silica and iron between Streams 4 and 11:

		_			
				_	
	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
NH3	352 ppm		352 ppm	[-	352 ppm

Id., highlighting added. Consequently, *Maimoni* selectively removes silica and iron from the brine. EX 1003, ¶284.

Additionally, the concentrations of silica and iron in the brine were reduced by about 90% between Stream 1 and Stream 11. EX 1004, at 16. As such, the clarified brine of *Maimoni* in Stream 11 is a "substantially silica free brine" as that phrase is used in the '117 patent. EX 1003, ¶285.

Moreover, silica post Stream 11 of *Maimoni* inherently coprecipitates with iron based on the disclosed processing conditions, thereby further reducing the concentration of silica to well below the reported concentration in Streams 18 and 21. Id., ¶¶292-293. When Maimoni adds Ca(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, shown below). Id., ¶294. A POSITA would further appreciate that by adding additional caustic soda, the process could be tuned such that silica and iron could be completely removed from the brine. Id., ¶295. Thus, Maimoni selectively removes silica and iron to produce a substantially silica free that includes manganese and zinc. Id., ¶296.

iv. removing the zinc from the substantially silica free brine (Claims 12 and 21);

Maimoni removes the zinc from the substantially silica free brine in Streams 11, 15 and 18 using precipitation:

39

		-					
	1		11		15		18
SiO2	230 ppm total 187 ppm solid		22 ppm				
Fe	055 and	2	20		26 ppm		13 ppm
Fe	255 ppm	2	26 ppm		333 ppm		17 ppm
Zn	333 ppm		333 ppm		775 ppm		39 ppm
Mn	775 ppm		775 ppm	************	56 ppm		6 ppm
Pb	70 ppm		56 ppm		182 ppm		182 ppm
Li	182 ppm	-	182 ppm		22.1%		22.1%
Inertia	22.1%	-	22.1%		777%		77.8%
H ₂ O	77.7%	1	77.1%		1.132		1.13
Specific grey	1.135		1.13		90		90
Temp. °C	93		92		195		195
Temp. °F	200		198		15		15
Flow, gpm	15		15		904	-	902
Flow, gph	900		901	-			
Flow, cfm	_	[05.40		8515
Flow, Ib/h	8523	T -	8508	-	8540		0010
Specific heat Btu/lb °F	0.85	Ī	0.85	-	0.85		0.85
Heat Btu/h	1.45 × 10 ⁶	† -	144 × 10 ⁶		1.41 X 10 ⁶	-	1.41 × 10 ⁶
Density	9.47 lb/gal	Ī	944 lb/gal		9.45 lb/gal	-	9.44 lb/ga
NH3	352 ppm	T -	352 ppm		352 ppm		35 ppm

EX 1004, at 16-17, highlighting added. As can readily be seen, the concentration of zinc is reduced in Stream 18, which occurs after the iron and silica have been selectively removed from the brine. *Id.* Consequently, *Maimoni* removes zinc from the brine. EX 1003, ¶299.

To the extent that "removing the zinc" is construed as removal by solvent extraction or ion exchange, the '117 patent admits that zinc removal using solvent extraction or ion exchange are prior art, namely using the resins and solvents of *Featherstone I.* EX 1011, Abstract, 4:18-34; VII(d), *supra*.

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. 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.).

Maimoni discloses removing zinc from the substantially silica free brine using precipitation, and *Featherstone I* discloses removing zinc from the substantially silica free brine using ion exchange and solvent extraction. Moreover, the substantially silica free brine of *Maimoni* could be readily utilized by the process of *Featherstone I* in order to remove zinc using ion exchange and solvent extraction. EX 1003, ¶370-373.

v. extracting manganese from the substantially silica free brine (Claims 12 and 21);

Similarly, *Maimoni* extracts manganese from the substantially silica free brine in Stream 15 using precipitation. EX 1004, at 16-17. After the silica and iron have been removed from the brine, Table 5 shows that the concentration of manganese is reduced in Stream 18. *Id.* Thus, *Maimoni* teaches "extracting manganese from the substantially silica free brine." EX 1003, ¶301. To the extent that "extracting manganese" is construed as removal by solvent extraction, the '117 patent states that manganese can be extracted from substantially silica free brines using the extraction processes and/or solvents disclosed by *Featherstone I* and/or *Featherstone II*. EX 1001, 11:6-10.

Like *Featherstone I* (EX 1011, 2:19-24; 6:56-59; 7:25-31), *Featherstone II* discloses diethyl-hexylphosphate (DEPHA or D2EPHA) and Cyanex 272 as exemplary organic solvents for the extraction of manganese. EX 1012, [0057].

As such, in addition to *Maimoni*'s disclosure of extracting manganese from the substantially silica free brine using precipitation, *Featherstone I* and *Featherstone II* clearly disclose extracting manganese from a substantially silica free brine using solvent extraction. EX 1003, ¶355-359.

vi. oxidizing the manganese to produce a manganese dioxide precipitate (Claim 12); and

Even though *Maimoni* does not teach "oxidizing the manganese to produce a manganese dioxide precipitate", it would have been obvious to combine *Maimoni* and *Featherstone II*. EX 1003, ¶374.

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. 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].

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

As such, in addition to *Maimoni*'s disclosure that electrolytic manganese dioxide is the targeted by-product, (EX 1006, at 13), *Featherstone II* 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]; EX 1003, ¶¶342-347.

vii. recovering the manganese dioxide precipitate (Claim 12).

As admitted by the '117 patent, manganese dioxide precipitates can be separated or recovered by filtration and "**other known means**". EX 1001, 9:1-3; 10:45-46; 12:41-44; 13:10-12, emphasis added. Consequently, methods for recovery of solid manganese dioxide are prior art to the invention of the '117 patent.

Even though *Maimoni* does not teach this step, *Featherstone II* clearly does. EX 1003, ¶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].

2. Claim 13 – Silica and Iron Removal

Maimoni discloses removing silica and then separating iron from manganese and zinc by selective precipitation of the respective hydrated oxides using lime and oxidizing ferrous to ferric iron by sparging air through the brine. EX 1004, at 16; EX 1003, ¶160. A 40% slaked lime slurry (Ca(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 (Fe(OH)₃) and/or ferric oxyhydroxide (FeOOH). EX 1004, at 16. The additional silica coprecipitates with the iron, especially ferric iron generated by the sparged Salton Sea geothermal brine in the iron reactor. *Id*.

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

 $4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$

The Fe3+ reacts with water to form ferric hydroxide, Fe(OH)3, or ferric oxyhydroxide hydrate, FeOOH*H2O:

 $Fe^{3+} + 3H_2O = Fe(OH)^3 + 3H^+ \text{ or } FeOOH^*H_2O + 3H^+$

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

EX 1003, ¶124.

Maimoni discloses that the feed brine from the Magmamax No. 1 well has an initial pH of between 5.2 and 6.1 (Table 1) or 5.6 (Table 2). EX 1004, at 9-10. *Maimoni* sparges the brine in the iron reactor with air (Stream 6), which generally reduces the pH of the brine in the iron reactor. EX 1003, ¶289. The reduction of the pH is offset by the introduction of calcium hydroxide (Stream 5) to the iron reactor. *Id.*

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, as required by Claim 12. Given the pH of the feed brine, these pH values occur as a result of the air oxidation and introduction of calcium hydroxide. *Id.*, ¶¶290-291.

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.

Accordingly, *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." EX 1003, ¶291.

3. Claim 14 – Zinc removal "by ion exchange"

Even though *Maimoni* does not teach this step, the '117 patent admits zinc removal from substantially silica free brine is known in the art. EX 1001, 10:28-37; VII(d), *supra*.

Plus, *Featherstone I* discloses that recovery of zinc from geothermal brines using ion exchange. EX 1011, Title; Abstract; VIII(c)(1)(iv), *supra*.

4. Claim 15 - Oxidizing manganese by "electrolytic deposition"

Featherstone II was admitted as prior art in the specification of the '117 patent, and discloses oxidizing manganese that has been extracted from a brine to produce manganese dioxide at the anode of an electrolysis cell. EX 1012, [0084]; VIII(c)(1)(vi), *supra*.

d. Ground 2: Claims 12, 14-15 and 21 are anticipated by and/or obvious over *Bourcier* (EX 1005) in view of AAPA and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).

- 1. Claims 12 and 21
 - i. A method for recovering zinc and manganese from a brine, the method comprising the steps of (Claims 12 and 21):

Bourcier discloses "Recovery of Minerals and Metals from Geothermal Brines", and that "the opportunities, the processes, the challenges, the current status,

the economics and the potential for recovery of minerals and metals from geothermal

fluids", namely recovering zinc and manganese from Salton Sea and other

geothermal brines. EX 1005, at Title and Abstract.

ii. providing a brine, said geothermal brine comprising manganese and zinc (Claims 12 and 21);

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.

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.

iii. selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc (Claims 12 and 21);

Bourcier clearly recognizes that silica which is a "ubiquitous component" of geothermal brines must be removed or reduced in concentration before mineral recovery. *Id.*, at 8, 12. *Bourcier* discusses that silica coprecipitates with iron using a process that combines lime addition and silica seeding: "The silica precipitated with this method has significant amounts of contaminants such as iron …". *Id.*, at 12. In discussing mineral extraction at the Salton Sea geothermal field, *Bourcier* further recognizes that "[s]ilica must be <u>removed</u> 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." EX 1005, at 12, emphasis added.

Accordingly, *Bourcier* removes or reduces silica and iron from the brine to produce a "substantially silica free brine" as that term is used in the '117 patent. EX 1003, ¶308.

iv. removing the zinc from the substantially silica free brine (Claims 12 and 21);

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)." EX 1005, at 4; *see also*:

The metal-rich geothermal fluids are being mined for their zinc content by CalEnergy Minerals. ... The brine is passed over an anionic ion exchange bed (IX) to extract the zinc... The zinc is then extracted from the eluate in a solvent extraction process (SX) utilizing a water immiscible cationic extractant. ... After separation of the SX extractant, the zinc sulfate solution undergoes electrowinning to produce metallic zinc.

Id., at 11-12. As noted above in connection with this claim, *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. EX 1003, ¶311. Thus, *Bourcier* clearly teaches removing the zinc from the substantially silica free brine.

v. extracting manganese from the substantially silica free brine (Claims 12 and 21);

Bourcier also discloses extracting manganese from the substantially silica free brine by solvent extraction:

CalEnergy has investigated methods for extracting manganese from their brines. ... 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.

EX 1005, at 13, emphasis added. Like zinc, *Bourcier* clearly extracts manganese from the substantially silica free brine. EX 1003, ¶312.

vi. oxidizing the manganese to produce a manganese dioxide precipitate (Claim 12); and

Bourcier discloses extracting manganese from the brine to produce electrolytic manganese dioxide for use in batteries. EX 1005, at 11, emphasis added.

To the extent that *Bourcier* is interpreted to not teach "oxidizing the manganese to produce a manganese dioxide precipitate", it would have been obvious to combine *Bourcier* and *Featherstone II*. EX 1003, ¶374-375.

In addition to *Bourcier*'s disclosure that electrolytic manganese dioxide is the targeted by-product, (EX 1006, at 13), *Featherstone II* 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]; VIII(c)(1)(vi), *supra*.

vii. recovering the manganese dioxide precipitate (Claim 12).

As admitted by the '117 patent, manganese dioxide precipitates can be separated or recovered by filtration and "**other known means**". EX 1001, 9:4-7; 10:51-52; 12:46-49; 13:15-17, emphasis added. Consequently, methods for recovery of solid manganese dioxide are prior art to the invention of the '117 patent.

Bourcier discloses manganese that is recovered and processed to produce electrolytic manganese dioxide for use in batteries. EX 1005, at 11.

To the extent that *Bourcier* is interpreted to not teach this step, it would have been obvious to combine *Bourcier* and *Featherstone II*. EX 1003, ¶374.

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." EX 1012, [0086].

A POSITA would readily appreciate that manganese dioxide of *Bourcier* could have been recovered like *Featherstone II*. EX 1003, ¶¶374-375.

2. Claim 14 – Zinc removal "by ion exchange"

Bourcier teaches removing zinc from the substantially silica free brine by ion exchange. EX 1005, at 11-12; VIII(d)(1)(iv), *supra*.

Moreover, the '117 patent admits zinc removal from substantially silica free brine is known in the art. VIII(c)(3), *supra*.

Plus, *Featherstone I* discloses that recovery of zinc from geothermal brines using ion exchange. EX 1011, Title; Abstract; VIII(c)(1)(iv), *supra*.

3. Claim 15 - Oxidizing manganese by "electrolytic deposition"

Bourcier discloses manganese that is recovered and processed to produce electrolytic manganese dioxide for use in batteries. EX 1005, at 11. As such, *Bourcier* teaches producing manganese dioxide by electrolytic deposition of Claim 15. EX 1003, ¶313.

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; VIII(c)(1)(vi), *supra*.

- e. Ground 3: Claims 12-15 and 21 are anticipated by and/or obvious over *Christopher* (EX 1006) in view of AAPA and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).
 - 1. Claims 12 and 21
 - i. A method for recovering zinc and manganese from a brine, the method comprising the steps of (Claims 12 and 21):

Christopher discloses recovery of mineral values from geothermal brines, *e.g.*, "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, emphasis added.

ii. providing a brine, said brine comprising manganese and zinc (Claims 12 and 21);

Christopher discloses post-flash geothermal brines from Sinclair No. 4 that include manganese and zinc. *Id.*, at 8. *Christopher* provides the post-flash geothermal brines for heavy metal precipitation in Table 3 which includes manganese, and for sequential brine purification in Figure 20. *Id.*, at 12, 42.

iii. selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc (Claims 12 and 21);

Christopher selectively removes silica and iron from the geothermal brine by precipitation to produce a substantially silica free brine that contains manganese and zinc. Initially, *Christopher* flashes the Sinclair No. 4 brine, which reduces the silica concentration by about 95% in the post-flash brine relative to the feed brine. EX 1003, ¶318.

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.

Since silica and iron are known to coprecipitate together, the iron removal process of *Christopher* will also inevitably precipitate silica from the post-flash brine. EX 1003, ¶326. *Christopher* oxidizes the brine with oxygen and controls the

pH of the brine between 5.5 and 7 with lime, and as a result, *Christopher* necessarily coprecipitates silica and iron from the geothermal brine to produce a substantially silica free brine as that phrase is used in the '117 patent. *Id.*, ¶327.

Silica in the pre-flash brine and post-flash brine of *Christopher* inherently coprecipitates with iron based on the disclosed pH range between 5.5 and 7 and oxidizing processing conditions, thereby reducing the concentration of silica in the clarified brine to well below the reported silica concentration levels. *Id.*, ¶328. 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. *Id.*, ¶329.

Like *Christopher*, the '117 patent discloses treating a brine by precipitating silica with iron. EX 1001, 6:35-50. The '117 patent acknowledges one common silica management method, a method identical to the method disclosed by *Christopher*, wherein iron (II) salt in the brine is oxidized to iron (III) hydroxide using oxygen or air as the oxidant and lime to control the pH range of between 4 and 7. *Id.* In addition, like *Christopher*, Examples 1-3 of the '117 patent precipitate iron and silica from a synthetic brine by oxidizing the ferrous iron to ferric iron using air and controlling the pH with the addition of a slurry of calcium hydroxide or lime. *Id.*, 16:55-18:8. When the brine is aerated, the ferrous ion is converted into the ferric

ion, and the Fe^{3+} reacts with water to form ferric hydroxide, $Fe(OH)_3$, or ferric oxyhydroxide hydrate, $FeOOH^*H_2O$. Once ferric oxyhydroxide hydrate is generated, it reacts quantitatively with silica (as silicic acid) to form an insoluble ferric silicate precipitate. EX 1003, ¶181.

A POSITA could adjust the parameters of the process without undue experimentation to selectively remove silica and iron from the geothermal brine to produce a brine with an arbitrarily low silica concentration. *Id.*, ¶182. Consequently, 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 and iron concentrations in the pre-flash or post-flash brine by at least 95% in the Product Brine of Table 3 and/or in the Iron Precipitation Discharge Liquor (2) of Figure 20. *Id.*, ¶329. Accordingly, *Christopher* selectively 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. *Id.*, ¶327.

iv. removing the zinc from the substantially silica free brine (Claims 12 and 21);

Christopher removes the zinc from the substantially silica free brine. EX 1006, at 6-26, 42. Like 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 between the Feed Brine and the Product Brine. *Id.*, at 12. Similarly, in Figure 20, the zinc concentration in the Feed Brine (1) is reduced in the Iron

Precipitation Discharge Liquor (2) and is further reduced in the Manganese Precipitation Discharge Liquor (3), and still further reduced in the Product Brine (4). The precipitated zinc solids that are removed are filtered and washed to produce a Mixed Oxide Product (6). *Id.*, at 42. As such, *Christopher* discloses removing zinc from the substantially silica free brine. EX 1003, ¶331.

To the extent that "removing the zinc" is construed as removal by solvent extraction or ion exchange, the '117 patent admits that zinc removal using ion exchange and solvent extraction is prior art, namely using the resins and solvents of *Featherstone I.* EX 1011, Abstract, 4:18-34; VIII(c)(1)(iv), *supra*.

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. 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.*, 2:19-24; 6:56-59; 7:25-31.

Christopher discloses removing zinc from the substantially silica free brine using precipitation (EX 1006, at 16-17), and *Featherstone I* discloses removing zinc from the substantially silica free brine using ion exchange and solvent extraction. EX 1011, Abstract. Moreover, the substantially silica free brine of *Christopher* could be readily fed to the process of *Featherstone I* in order to remove zinc using ion exchange and solvent extraction. EX 1003, ¶¶374-375.

v. extracting manganese from the substantially silica free brine (Claims 12 and 21);

Christopher discloses extracting manganese from the substantially silica free brine by precipitation. EX 1006, at 6-26, 42. Manganese is precipitated from the Sinclair No. 4 geothermal brine by using air and lime. In Table 3, the manganese concentration is reduced between the Feed Brine and the Product Brine. *Id.*, at 12. Similarly, in Figure 20, the manganese concentration in the Feed Brine (1) remains constant in the Iron Precipitation Discharge Liquor (2), which is then reduced in the Manganese Precipitation Discharge Liquor (3) and the Product Brine (4). The precipitated manganese solids are removed and washed to produce a Mixed Oxide Product (6). *Id.*, at 42. As such, *Christopher* discloses extracting manganese from the substantially silica free brine. EX 1003, ¶335.

The '117 patent admits that manganese can be extracted from substantially silica free brines using the extraction processes and/or solvents disclosed by *Featherstone I* and/or *Featherstone II*. See VII(e), *supra*. Like *Featherstone I*, *Featherstone II* discloses diethyl-hexylphosphate (DEPHA) and Cyanex 272 as exemplary organic solvents for the extraction of manganese. EX 1012, [0057].

As such, in addition to *Christopher*'s disclosure of extracting manganese from the substantially silica free brine using precipitation, *Featherstone I* and *Featherstone II* admittedly disclose extracting manganese from a substantially silica free brine using solvent extraction. EX 1003, ¶¶355-359.

vi. oxidizing the manganese to produce a manganese dioxide precipitate (Claim 12); and

Even though *Christopher* does not teach "oxidizing the manganese to produce a manganese dioxide precipitate", it would have been obvious to combine *Christopher* and *Featherstone II. Id.*, ¶¶374-375.

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. 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].

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

Featherstone II clearly discloses oxidizing manganese that has been extracted from a brine to produce manganese dioxide at the anode of an electrolysis cell. EX 1009, 9:40-47; EX 1012, [0084].

vii. recovering the manganese dioxide precipitate (Claim 12).

As admitted by the '117 patent, manganese dioxide precipitates can be separated or recovered by filtration and "**other known means**". EX 1001, 9:1-3; 10:45-46; 12:41-44; 13:10-12, emphasis added. Consequently, methods for recovery of solid manganese dioxide are prior art to the invention of the '117 patent.

Even though *Christopher* does not teach this step, *Featherstone II* clearly does. EX 1003, ¶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].

2. Claim 13 – Silica and Iron Removal

Christopher provides iron (III) at a pH of between about 4.5 and 6 and precipitating the silica. Initially, *Christopher* flashes the Sinclair No. 4 brine, which reduces the silica concentration by about 95% in the post-flash brine. VIII(e)(1)(ii), *supra*; EX 1003, ¶318.

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 between 4.5 and 6 to produce an "iron free brine". EX 1006, at 16-22 and 42, emphasis added.

Moreover, since silica and iron are known to coprecipitate, the iron removal process of *Christopher* will also inevitably further precipitate silica from the post-flash brine. EX 1003, ¶¶180-181, 326. *Christopher* oxidizes the brine with oxygen and controls the pH of the brine between 4.5 and 6 with lime, and as a result, *Christopher* necessarily coprecipitates silica and iron from the geothermal brine to produce a substantially silica and iron free brine as that phrase is used in the '117 patent. *Id.*, ¶327.

3. Claim 14 – Zinc removal "by ion exchange"

The '117 patent admits zinc removal from substantially silica free brine is known in the art. VIII(c)(3), *supra*.

Plus, *Featherstone I* discloses that recovery of zinc from geothermal brines using ion exchange. EX 1011, Title; Abstract.

4. Claim 15 - Oxidizing manganese by "electrolytic deposition"

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.

- f. Ground 4: Claims 12-15 and 21 are obvious over *Maimoni* (EX 1004) and/or *Bourcier* (EX 1005) and/or *Christopher* (EX 1006) in view of *Jost* (EX 1007) and/or *Wilkins* (EX 1008) and/or *Brown* (EX 1010), and in further view of *Geisler* (EX 1009) and/or *Featherstone I* (EX 1011) and/or *Featherstone II* (EX 1012).
 - 1. Claims 12 and 21
 - i. A method for recovering zinc and manganese from a brine, the method comprising the steps of (Claims 12 and 21):

Maimoni discloses a method for recovering zinc and manganese from a brine.

VIII(c)(1)(i), supra.

Bourcier discloses a method for recovering zinc and manganese from a brine.

VIII(d)(1)(i), supra.

Christopher discloses a method for recovering minerals, including zinc and

manganese, from a brine. *VIII*(e)(1)(i), *supra*.

ii. providing a brine, said brine comprising manganese and zinc (Claims 12 and 21);

Maimoni discloses providing a brine having zinc and manganese. VIII(c)(1)(ii), supra.

Bourcier discloses providing a brine having zinc and manganese. *VIII*(d)(1)(ii), *supra*.

Christopher discloses providing a brine having zinc and manganese. VIII(e)(1)(ii), supra.

iii. selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc (Claims 12 and 21);

Maimoni, Bourcier, and *Christopher* each individually disclose selectively removing silica and iron from the brine to produce a substantially silica free brine. *VIII*(c)(1)(iii), VIII(d)(1)(iii) and VIII(e)(1)(iii), *supra*.

To the extent that *Maimoni*, *Bourcier*, and *Christopher* are interpreted to not each individually disclose selectively removing silica and iron, Petitioner submits that *Bourcier* and/or *Christopher* in combination with *Maimoni* clearly disclose selectively removing silica and iron from the brine to produce a substantially silica and iron free brine.

Bourcier and *Maimoni* recognize the importance of reducing or eliminating iron silicate scale from geothermal brines before mineral recovery. *Maimoni* states that silica and iron scale control and removal is a key part of any process for handling Salton Sea geothermal brines (EX 1004, at 10, 22), and *Bourcier* states that "[s]ilica must be removed from the fluid for the zinc extraction process to be successful." EX 1005, at 12.

If, however, *Maimoni, Bourcier*, and/or *Christopher* are somehow interpreted to not teach the "substantially silica free brine", it would have been obvious to combine *Maimoni, Bourcier*, and/or *Christopher* with *Brown* and/or *Jost* and/or *Wilkins* to achieve the substantially silica free brine. EX 1003, ¶370.

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." EX 1010, 3:54-59. *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.

Jost teaches a process for stabilizing silica-rich geothermal brine to prevent silica scaling. EX 1007, Abstract. The process taught by *Jost* includes:

[S]electively 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. "[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. EX 1003, ¶364. Like the substantially silica free brine of *Maimoni*, the processing conditions of *Jost* produces a substantially silica free brine. *Id*.

Like *Jost, Wilkins* is directed at a process for the removal of silica from geothermal brine. EX 1008, Title. *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. *Wilkins* explains that "[t]he filtrate from filter 23 flows through line 25 to be disposed of, as in brine disposal well 26." *Id.*, 5:55-56. Based on the pH and oxidizing conditions of *Wilkins*, a substantially silica free brine is produced by *Wilkins*, as set forth in curve 17 of Figure 2:



Id., highlighting added. In view of the foregoing, *Wilkins* teaches "selectively removing silica and iron from the geothermal brine to produce a substantially silica free brine." EX 1003, ¶367.

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. *Id.*, ¶370. 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. *Id.*, ¶371. A POSITA confronted with the problem of recovering minerals (*e.g.*, zinc and manganese) from geothermal brines would understand that silica and iron removal prior to mineral recovery may be achieved by modifying the processes of any 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*. *Id.*, ¶372.

iv. removing the zinc from the substantially silica free brine (Claims 12 and 21);

Maimoni discloses removing the zinc from the substantially silica free brine by precipitation. VIII(c)(1)(iv), *supra*. *Bourcier* discloses removing the zinc from the substantially silica free brine using ion exchange followed by solvent extraction and electrowinning. VIII(d)(1)(v), *supra*.

Christopher precipitates the zinc from the substantially silica free brine. *VIII*(e)(1)(iv), *supra*.

Featherstone I removes zinc from the substantially silica free brine using ion exchange followed by solvent extraction. VIII(c)(1)(v), VIII(d)(1)(v) and VIII(e)(1)(v), *supra*.

Moreover, *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 (*Id.*, Figure 1, Block 2), and then preferentially extracts lead (*Id.*, Block 3), then zinc (*Id.*, Blocks 6-8) and then manganese (*Id.*, Blocks 9-11) in that order using solvent extraction ("SX") followed by electrowinning ("EW"). *Id.*, at Abstract. *Geisler's* aqueous solution or leachate is a "brine" as that term is defined in the '117 patent. EX 1003, ¶¶196, 349.


EX 1009, at Figure 1. "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.

Similarly, *Brown* discloses a "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; *see also* 3:15-21; 4:15-18. "After substantially all silica is removed," zinc is then removed from the geothermal brine using solvent extraction as shown in Figure 1. *Id.*, 2:46-49.

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. *Id.*, ¶359. 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. As such, a POSITA 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. *Id.*, ¶¶360-361.

Moreover, a POSITA who was seeking to solve the problem of the '117 patent would recognize that the processes of *Maimoni*, *Christopher*, *Bourcier*, *Brown*, *Jost* and/or *Wilkins* selectively remove silica and iron, and leave manganese and zinc for subsequent mineral recovery. A POSITA would further recognize that zinc could be removed by precipitation by following the teachings *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 combination merely substitutes the zinc removal steps of *Maimoni* and/or *Christopher* with that of *Bourcier*, *Featherstone I*, *Featherstone I*, *Brown* and/or *Geisler* to yield predictable results. *Id.*, ¶¶373-377.

v. extracting manganese from the substantially silica free brine (Claims 12 and 21);

Maimoni discloses extracting manganese from the substantially silica free brine by precipitation. VIII(c)(1)(v), *supra*.

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Bourcier discloses extracting manganese from the substantially silica free brine using solvent extraction. VIII(d)(1)(v), *supra*.

Christopher precipitates manganese from the substantially silica free brine. VIII(e)(1)(v), *supra*.

Featherstone I and *Featherstone II* disclose extracting manganese from the substantially silica free brine by solvent extraction. VIII(c)(1)(v), VIII(d)(1)(v) and VIII(e)(1)(v), *supra*.

Geisler preferentially and sequentially extracts manganese using solvent extraction followed by electrowinning after removing any interfering minerals and metals. EX 1009, at Abstract, Figure 1. *Geisler* teaches extracting manganese from a substantially silica and iron-free brine using solvent extraction (Blocks 9-11) after zinc removal (Blocks 6-8).



Id., at Figure 1.

As discussed in VIII(f)(1)(v), *Brown* discloses that "[a]fter substantially all silica is removed," manganese is separated from the geothermal brine using solvent extraction as shown in Figure 1. EX 1010, 2:46-49.

To the extent the asserted references are interpreted to not disclose the limitations of this step, given the similarities in the subject matter and teachings from *Maimoni, Bourcier, Christopher, Featherstone I, Featherstone II, Brown*, and *Geisler*, it would have been obvious for a POSITA to combine teachings from one reference with teachings from another. EX 1003, ¶367. A POSITA would have been motivated to combine *Maimoni, Bourcier, Christopher, Featherstone I, Featherstone I, Featherstone II, Brown*, and *Geisler* to extract manganese from a geothermal brine that has been pretreated to remove silica and other fouling constituents as in *Maimoni* and/or *Brown* and/or *Jost* and/or *Wilkins. Id.*, ¶368.

A POSITA who was seeking to solve the problem of the '117 patent and who had knowledge of *Maimoni*, *Bourcier*, *Christopher*, *Brown*, *Featherstone I*, *Featherstone II*, *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 manganese extraction steps of *Maimoni*, *Bourcier*, *Christopher*, *Featherstone I*, *Featherstone II*, *Brown* and/or *Geisler*. *Id.*, ¶372.

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 recovery by the method of *Maimoni*, *Bourcier*, *Christopher*, *Featherstone I*, *Featherstone II*, *Brown* and/or *Geisler*. *Id.*, ¶370.

A POSITA would recognize that manganese could be extracted by precipitation by following the teachings *Maimoni* and/or *Christopher* or could be extracted by solvent extraction and ion exchange by following the teachings of *Bourcier, Featherstone I, Featherstone II, Brown* and/or *Geisler*. This merely substitutes the manganese extraction steps of *Maimoni* and/or *Christopher* with that of *Bourcier, Featherstone I, Featherstone II, Brown* and/or *Geisler* to yield predictable results. *Id.*, ¶370-373.

vi. oxidizing the manganese to produce a manganese dioxide precipitate (Claim 12); and

Geisler discloses oxidizing manganese by electrowinning to produce a manganese dioxide precipitate EX 1009, 9:20-24; Claim 13; Figure 1. *Geisler* describes electrowinning at Box 10 of Figure 1. "The MnSO₄ 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 MnO₂." *Id.*, 9:20-24; Claim 13.

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

$MnSO_4 + 2H_2O \rightarrow MnO_2 + 2H^+ + 2H_2SO_4 + 2e^-$

Id., 9:40-47, emphasis added. In Example 5, *Geisler* recovered the dissolved Mn at the anode as MnO₂ with a purity of 99.99%. *Id.*, 14:50-62.

Featherstone II also disclose oxidizing manganese by electrowinning to produce a manganese dioxide precipitate. EX 1014, [0022], [0084]; VIII(c)(1)(vi), VIII(d)(1)(vi), VIII(e)(1)(vi), *supra*.

vii. recovering the manganese dioxide precipitate (Claim 12).

Bourcier discloses manganese that is recovered and processed to produce electrolytic manganese dioxide for use in batteries. EX 1005, at 11; VIII(d)(1)(viii).

Geisler discloses that the solid phase (p) from the electrowinning circuit Box 10 is washed and dried. *Id.*, 9:37-40. Moreover, "[t]he MnO₂ was extracted from the discharge slurry by means of a 1 μ m filter and was found to have a purity of 99.99%." EX 1009, 14:58-62.

Featherstone II discloses recovering the manganese dioxide precipitate "using mechanical forces such as agitation, flexing, scraping, etc. Finally, the manganese dioxide may be ground, milled and neutralized using known methods." EX 1014, [0086]; VIII(c)(1)(vii); VIII(d)(1)(vii); VIII(e)(1)(vii).

2. Claim 13 – Silica and Iron Removal

Maimoni and *Christopher* both disclose providing iron (III) at a pH of between about 4.5 and 6 and precipitating the silica. *VIII*(c)(2); VIII(e)(2), *supra*. If *Maimoni* and/or *Christopher* are somehow interpreted to not teach the limitations of Claim 13, it would have been obvious to combine *Maimoni* and/or *Christopher* with *Jost* and/or *Wilkins* to provide iron (III) at a pH of between about 4.5 and 6 and precipitating the silica. EX 1003, ¶369.

As discussed above in VIII(f)(1)(iii), a POSITA who was seeking to reduce silica and iron would find *Jost* to be especially relevant. *Jost* discloses that silica is preferably removed by providing a supply of ferric ions, which then combine with silica in the brine. EX 1007, Abstract. *Jost* further notes that ""[t]he ferric ion content of an iron-deficient brine may be augmented by adding ferric and/or ferrous ions to the brine." *Id.*, Abstract; 9:55-59. *Jost* further discloses that the geothermal feed brine has a pH of about 4.5 to 6.0 (*Id.*, 11:40-49; Claims 1 and 17), and 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	2000 to 3000
content, ppm	
Ferric ion	5 to 60
content, ppm	.:

Id., 11:67-12:10, emphasis added.

Accordingly, *Jost* provides iron (III) at a pH of between about 4.5 and 6 and precipitating the silica. EX 1003, ¶364.

Like *Jost, Wilkins* is directed at a process for the removal of silica from geothermal brine. EX 1008, Title. *Wilkins* discloses a portion of the brine and sludge may be recycled back to the reaction chamber where the ferrous hydroxide is oxidized to ferric hydroxide, which form a precipitate that is less likely to stick on equipment surfaces. *Id.*, 5:45-50. The pH of the brine is controlled using ammonium hydroxide between 6.0 and 7.0. *Id.*, 4:13-24; Claim 3; Figure 2. As such, *Wilkins* discloses providing iron (III) at a pH of between about 4.5 and 6 and precipitating the silica. EX 1003, ¶364.

3. Claim 14 – Zinc removal "by ion exchange"

Bourcier teaches removing zinc from the substantially silica free brine by ion exchange. EX 1005, at 11-12; VIII(d)(2).

Moreover, the '117 patent admits zinc removal from substantially silica free brine is known in the art. VIII(c)(3), *supra*.

Plus, *Featherstone I* discloses that recovery of zinc from geothermal brines using ion exchange. EX 1011, Title; Abstract.

4. Claim 15 - Electrolytic Manganese Dioxide

Bourcier discloses manganese that is recovered and processed to produce electrolytic manganese dioxide for use in batteries. EX 1005, at 11; VIII(d)(3).

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Geisler teaches a $MnSO_4$ strip liquor (n) is treated (10) by electrowinning that deposits on the anode as 99.99% pure MnO_2 or electrolytic manganese dioxide (EMD). EX 1009, 9:20-24; 14:49-55; Claim 13; VIII(f)(1)(vi).

Featherstone II also discloses a "process for producing electrolytic manganese dioxide from geothermal brines" using electrolytic deposition. EX 1012, Title; VIII(f)(1)(vi).

IX. CONCLUSION

For the foregoing reasons, Petitioner has demonstrated a reasonable likelihood that Claims 12-15 and 21 of the '117 patent are anticipated and/or obvious in view of the prior art. Accordingly, Petitioner respectfully requests *inter partes* review of the Challenged Claims of the '117 patent.

Respectfully submitted,

CROWE & DUNLEVY, P.C.

Dated: October 1, 2019

<u>/Shawn M. Dellegar/</u> Shawn M. Dellegar, Reg. No. 58,994

ATTORNEYS FOR PETITIONER ENERGYSOURCE MINERALS, LLC

CERTIFICATE OF COMPLIANCE

Pursuant to 37 C.F.R. § 42.24(a) and (d), the undersigned hereby certifies that the above-captioned Petition for *Inter Partes* Review of U.S. Patent No. 9,057,117 complies with the type-volume limitation of 37 C.F.R. § 42.24(a)(1)(i) permitting a petition of up to 14,000 words because, exclusive of the exempted portions, the Petition contains 12,603 words, as identified by Microsoft Word's word-counting feature.

Respectfully submitted,

CROWE & DUNLEVY, P.C.

Dated: October 1, 2019

<u>/Shawn M. Dellegar/</u> Shawn M. Dellegar, Reg. No. 58,994

ATTORNEYS FOR PETITIONER ENERGYSOURCE MINERALS, LLC

CERTIFICATE OF SERVICE

Pursuant to 37 C.F.R. §§ 42.6(e) and 42.105(a), the undersigned hereby certifies that the above-captioned Petition for *Inter Partes* Review of U.S. Patent No. 9,057,117, including its supporting exhibits thereto, were served on October 1, 2019, via Federal Express Overnight Mail at the correspondence address of record for the '117 patent:

KILPATRICK TOWNSEND & STOCKTON LLP Mailstop: IP Docketing - 22 1100 Peachtree Street, Suite 2800 Atlanta, GA 30309

The undersigned further certifies courtesy services via electronic mail at the address(es) below:

jblackburn@kilpatricktownsend.com

Dated: October 1, 2019

<u>/Shawn M. Dellegar/</u> Shawn M. Dellegar, Reg. No. 58,994

CLAIM LISTING APPENDIX

No.	Claim Limitations
12.0	A method for recovering zinc 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.
13.	The method of claim 12 wherein the step of selectively removing silica and iron from the geothermal brine comprises providing iron (III) at a pH of between about 4.5 and 6 and precipitating silica.
14.	The method of claim 12 wherein the lithium chloride is selectively removed from the substantially silica free brine by ion exchange.
15.	The method of claim 12 wherein the step of oxidizing the manganese to produce manganese dioxide comprises electrolytic deposition.
21.0	A method for recovering zinc from a brine, the method comprising the steps of:
21.1	providing a brine, said brine comprising manganese and zinc;
21.2	selectively removing silica and iron from the brine to produce a substantially silica free brine that includes manganese and zinc;
21.3	removing the zinc from the substantially silica free brine;
21.4	extracting manganese from the substantially silica free brine.