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(54) **METHODS OF PROCESSING SOLUTIONS OF POTASSIUM SULFATE AND MAGNESIUM SULFATE, METHODS OF PRODUCING POTASSIUM SULFATE, AND RELATED SYSTEMS**

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(51) **Int. Cl.**
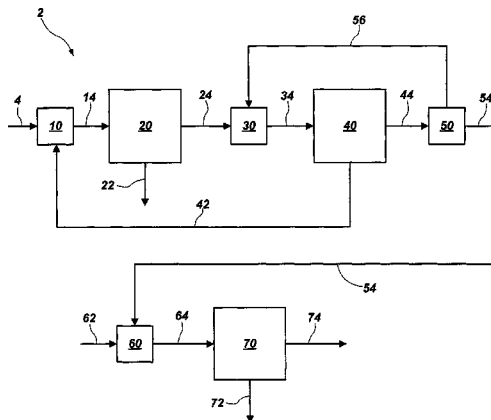   *C01D 5/00* (2006.01)
        C01D 5/16 (2006.01)
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(52) **U.S. Cl.**
        CPC *C01D 5/12* (2013.01); *B01D 9/0036* (2013.01); *B01D 9/02* (2013.01); *C01D 5/00* (2013.01); *C01D 5/10* (2013.01); *C01D 5/16* (2013.01)

(58) **Field of Classification Search**
        CPC C01D 5/16; C01D 5/00; B01D 9/02; B01D 9/0036
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        See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

| 1,794,552 A | 3/1931 | Schoch |
| 1,812,497 A | 6/1931 | Fletcher |

(Continued)

FOREIGN PATENT DOCUMENTS

DE	102007058666 A1	6/2009
GB	1183938	3/1970
WO	2010150267 A1	12/2010

OTHER PUBLICATIONS

Conley et al., "Potash Salt from Texas New Mexico Polyhalite Deposits: Commercial Possibilities, Proposed Technology, and Pertinent Salt Solution Equilibria," U.S. Dept. of the Interior, Bulletin 459, Washington, DC, 1944, pp. i-251.

(Continued)

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(57) **ABSTRACT**

Methods of processing an aqueous solution comprising potassium sulfate and magnesium sulfate include crystallizing K_2SO_4, crystallizing recycle crystals, and mixing at least a portion of the recycle crystals with the aqueous solution. Systems for processing potassium sulfate and magnesium sulfate include a first crystallizer and a second crystallizer in fluid communication with the second mix tank. The second crystallizer is structured and adapted to precipitate recycle crystals from the concentrated liquor to form a potassium-depleted recycle brine. The recycle crystals precipitated in the second crystallizer have a composition suitable to be recycled to the first crystallizer to increase the production of SOP.

20 Claims, 13 Drawing Sheets

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    C01D 5/10   (2006.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,924,519 A	8/1933	Schoch	
1,939,174 A	12/1933	Kaselitz	
1,952,289 A	3/1934	Schoch	
2,020,322 A	11/1935	Lambert	
2,033,149 A	3/1936	Partridge et al.	
2,769,489 A	11/1956	Eckstrom	
2,860,951 A	11/1958	Cunningham	
2,862,788 A	12/1958	Stanley, Jr. et al.	
2,895,794 A	7/1959	Dancy et al.	
2,902,334 A	9/1959	Milne	
2,991,154 A	7/1961	Patzias	
3,004,826 A	10/1961	Marullo et al.	
3,058,806 A	10/1962	Karl	
3,110,561 A	11/1963	Henne et al.	
3,203,757 A	8/1965	Henne et al.	
3,271,106 A	9/1966	Nylander	
3,285,025 A	11/1966	Shaul	
3,396,086 A	8/1968	Starmer	
3,475,132 A	10/1969	Seifert et al.	
3,528,767 A	9/1970	Garrett	
3,547,597 A	12/1970	Hays	
3,617,243 A	11/1971	Neitzel	
3,630,713 A	12/1971	Adams et al.	
3,634,041 A	1/1972	Ryan et al.	
3,843,772 A	10/1974	Boeglin	
3,926,609 A	12/1975	Effmert et al.	
3,998,935 A	12/1976	Adams et al.	
4,026,696 A	5/1977	Young	
4,045,335 A	8/1977	Adams et al.	
4,183,738 A	1/1980	Carmon	
4,246,019 A	1/1981	Sokolov et al.	
4,277,253 A	7/1981	Walter et al.	
4,303,468 A	12/1981	Laguilharre et al.	
4,306,880 A	12/1981	Garrett	
4,334,885 A	6/1982	Harrison et al.	
4,500,336 A	2/1985	Van Hijfte et al.	
4,533,536 A	8/1985	Bichara et al.	
4,554,151 A	11/1985	Worthington et al.	
4,815,790 A	3/1989	Rosar	
5,057,208 A	10/1991	Hagedorn et al.	
5,078,779 A	1/1992	Van de Walle et al.	
5,102,441 A	4/1992	Zentgraf et al.	
5,246,273 A	9/1993	Rosar	
5,298,050 A	3/1994	McLaughlin et al.	
5,609,838 A	3/1997	Neuman et al.	
5,955,043 A	9/1999	Neuman et al.	
6,013,209 A	1/2000	Phinney	
6,143,271 A	11/2000	Holdengraber et al.	
6,251,346 B1	6/2001	Neuman et al.	
6,322,767 B1	11/2001	Neuman et al.	
6,428,759 B1	8/2002	Smith et al.	
6,576,206 B2	6/2003	Copenhafer et al.	
6,582,637 B1	6/2003	Phinney	
6,709,685 B1	3/2004	van Brempt et al.	
7,604,792 B2	10/2009	Fairchild	
8,802,048 B2 *	8/2014	Chastain et al.	423/551
2006/0032114 A1	2/2006	Krysiak et al.	
2006/0226051 A1	10/2006	Navarrette et al.	
2010/0031719 A1	2/2010	Hero et al.	
2010/0066153 A1	3/2010	Day et al.	
2013/0121900 A1	5/2013	Neuman et al.	
2014/0072507 A1	3/2014	Chastain et al.	

OTHER PUBLICATIONS

Felton, et al., "Producing Sulfate of Potash from Polyhalite with Cost Estimates," Gustayson Associates, Mar. 23, 2010, pp. 1-19.

Fragen, et al., "Extraction of Potash from Polyhalite," Industrial and Engineering Chemistry, Oct. 1933, vol. 25, No. 10, pp. 1153-1160.

Wollmann et al., "Heat of solution of polyhalite and its analogues at T = 298.15 K," J. Chem. Thermodynamics, 41 (2009) 484-488.

International Search Report and Written Opinion of the International Search Authority for PCT/US2013/059040, mailed Dec. 4, 2013, 10 pages.

J.M. Davidson et al, Potash from Polyhalite: Relation between Calcination Conditions and Extraction Behavior, Industrial and Engineering Chemistry. American Chemical Society, US. vol. 29. No. 4. Apr. 1, 1937. pp. 475-482. XP008150228. ISSN: 0019-7866. DOI: 10.1021/IE50328A027.

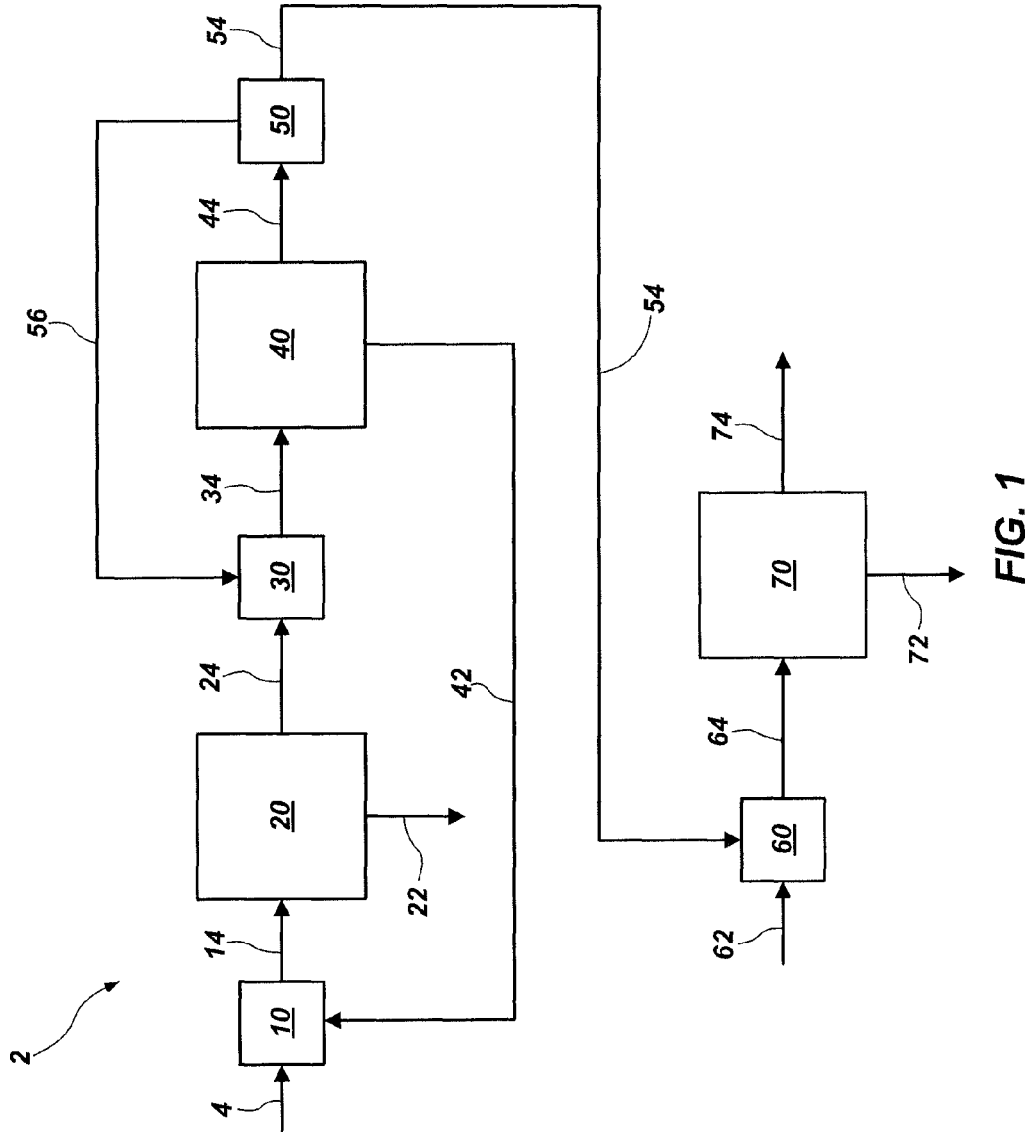Supplementary European Search Report for Application No. 12850346.3-2780286 PCT/US2012/063687, dated Jul. 14, 2015, 7 pages.
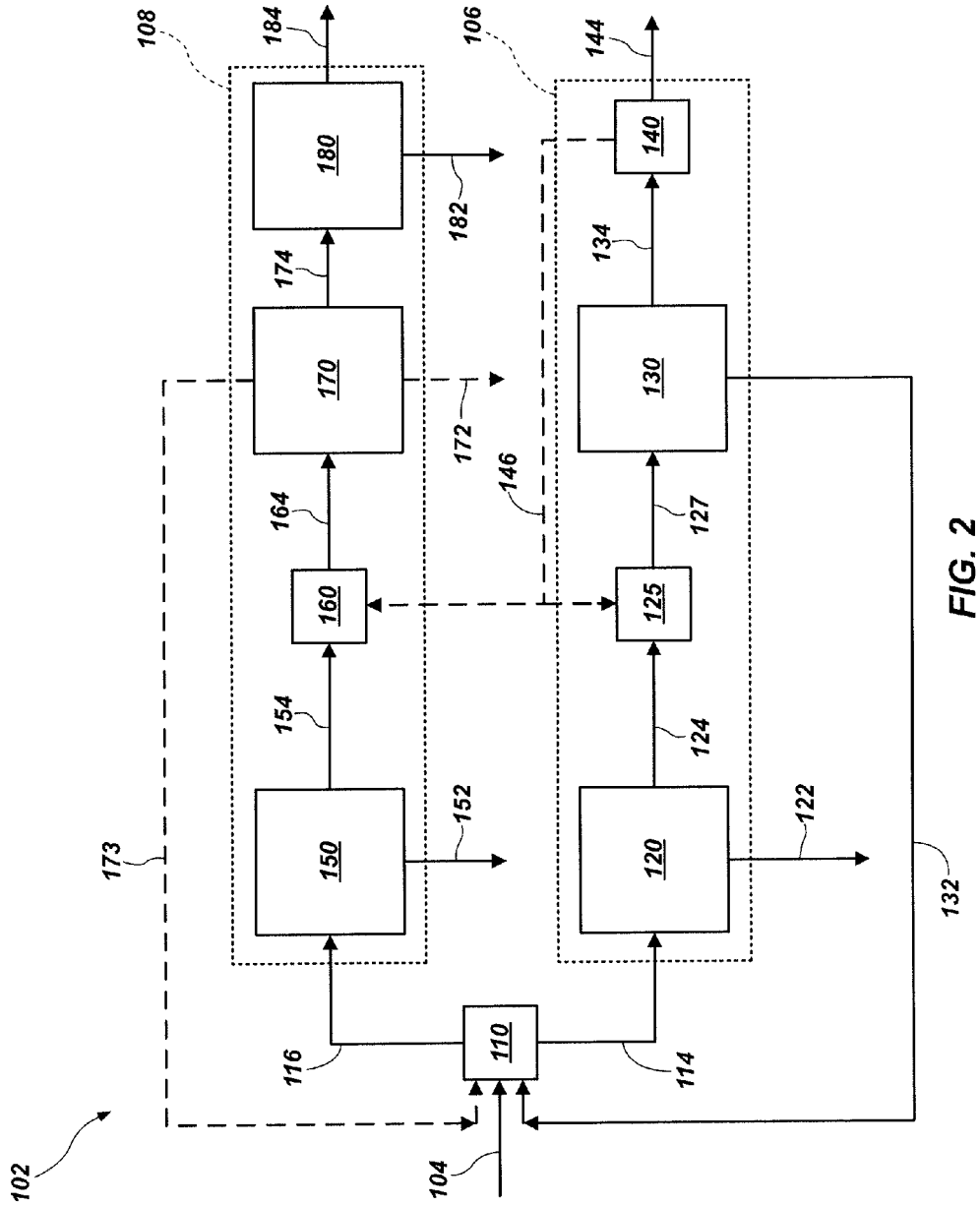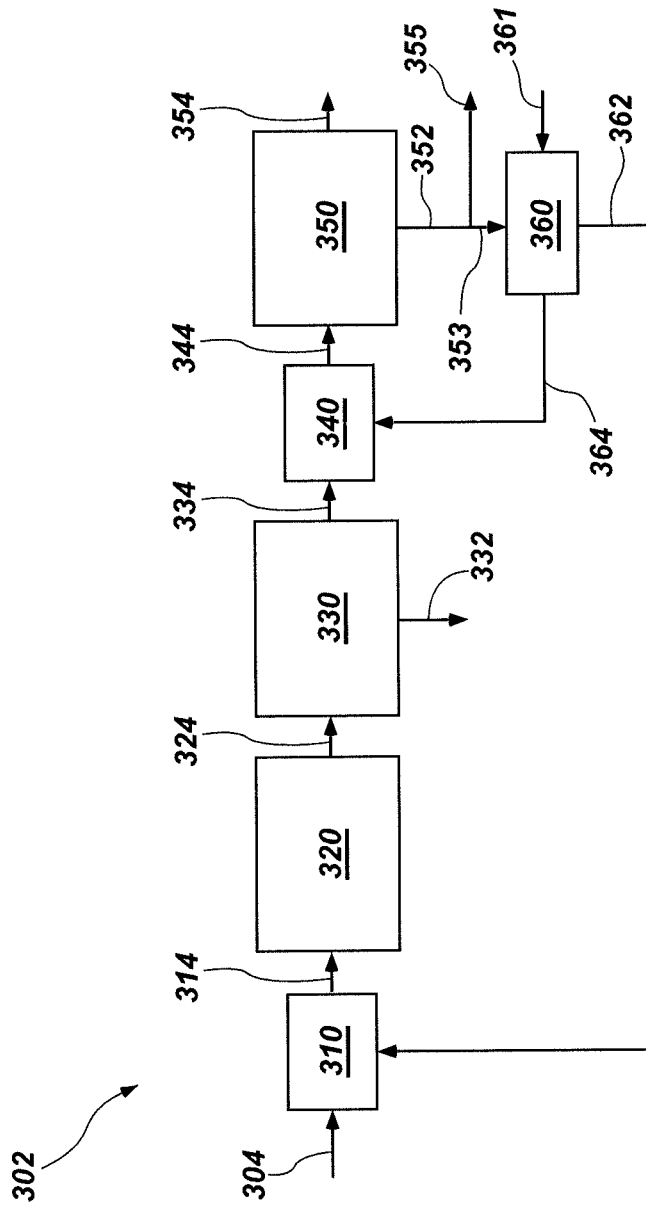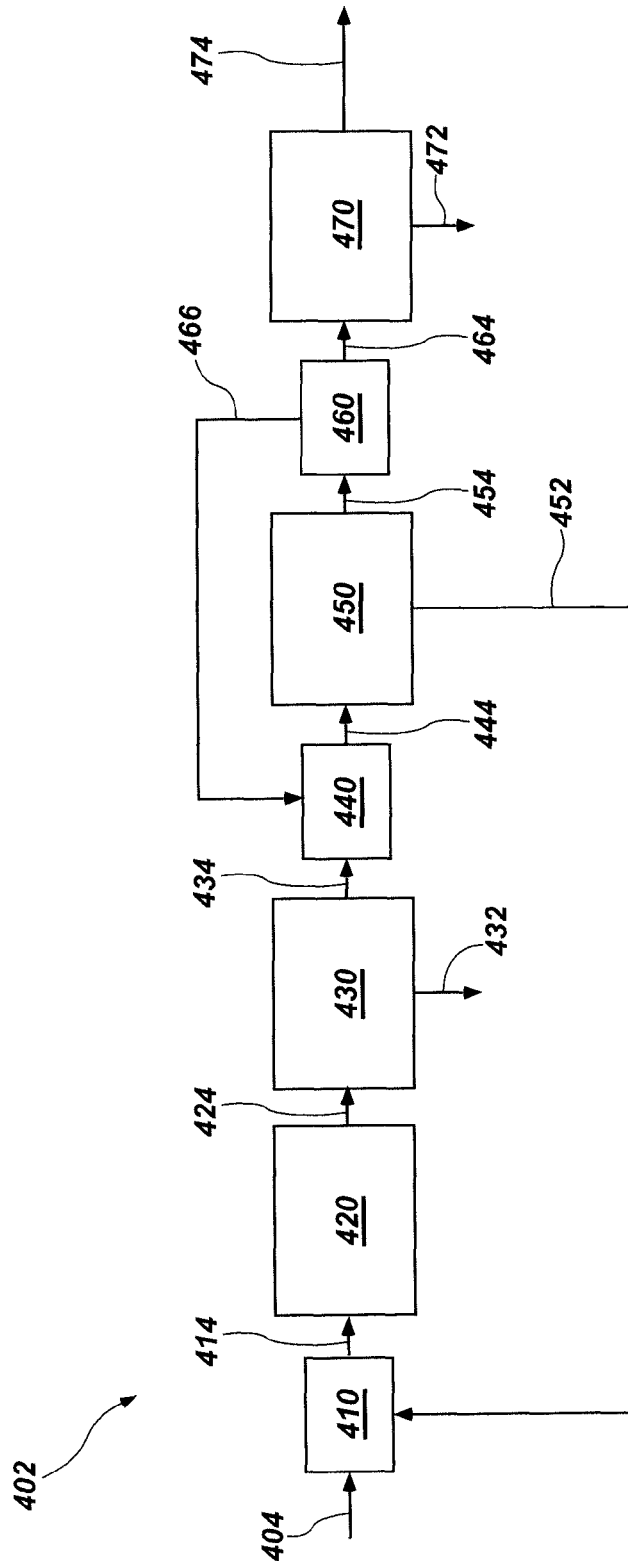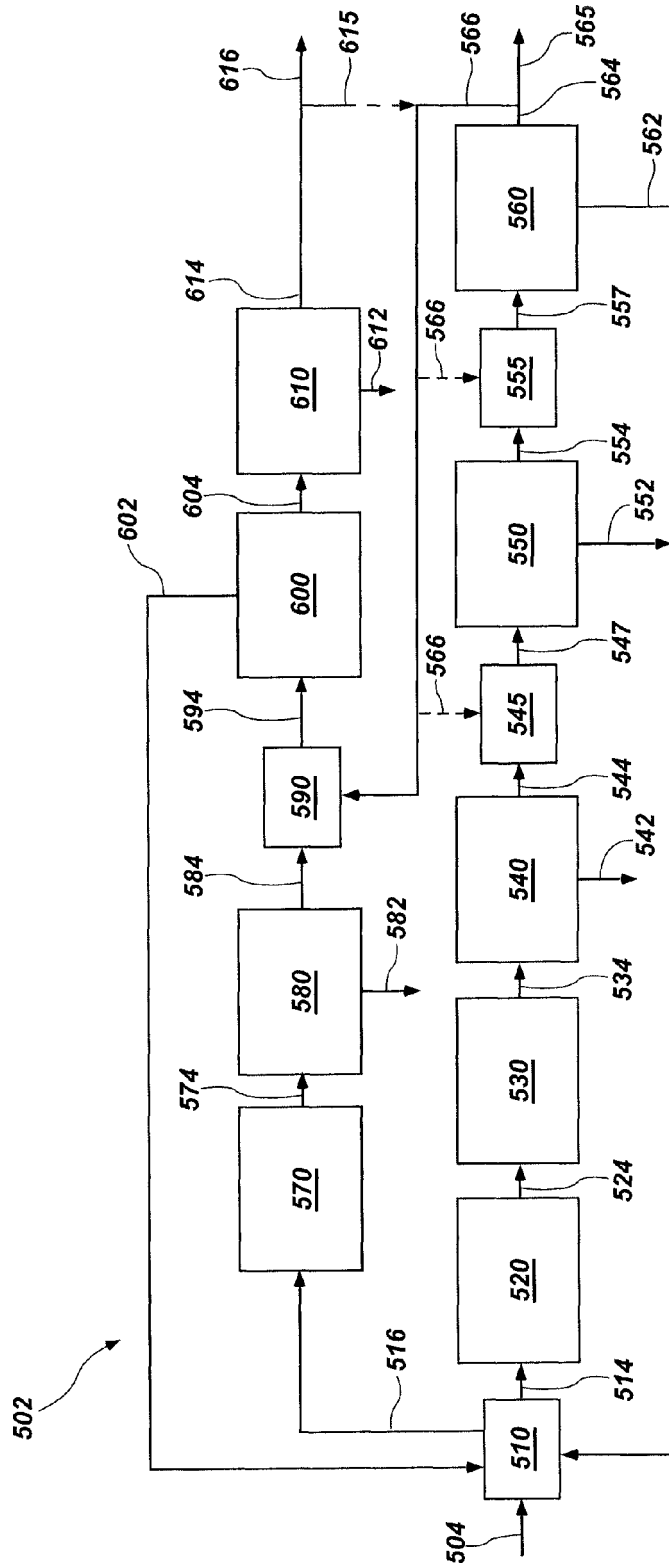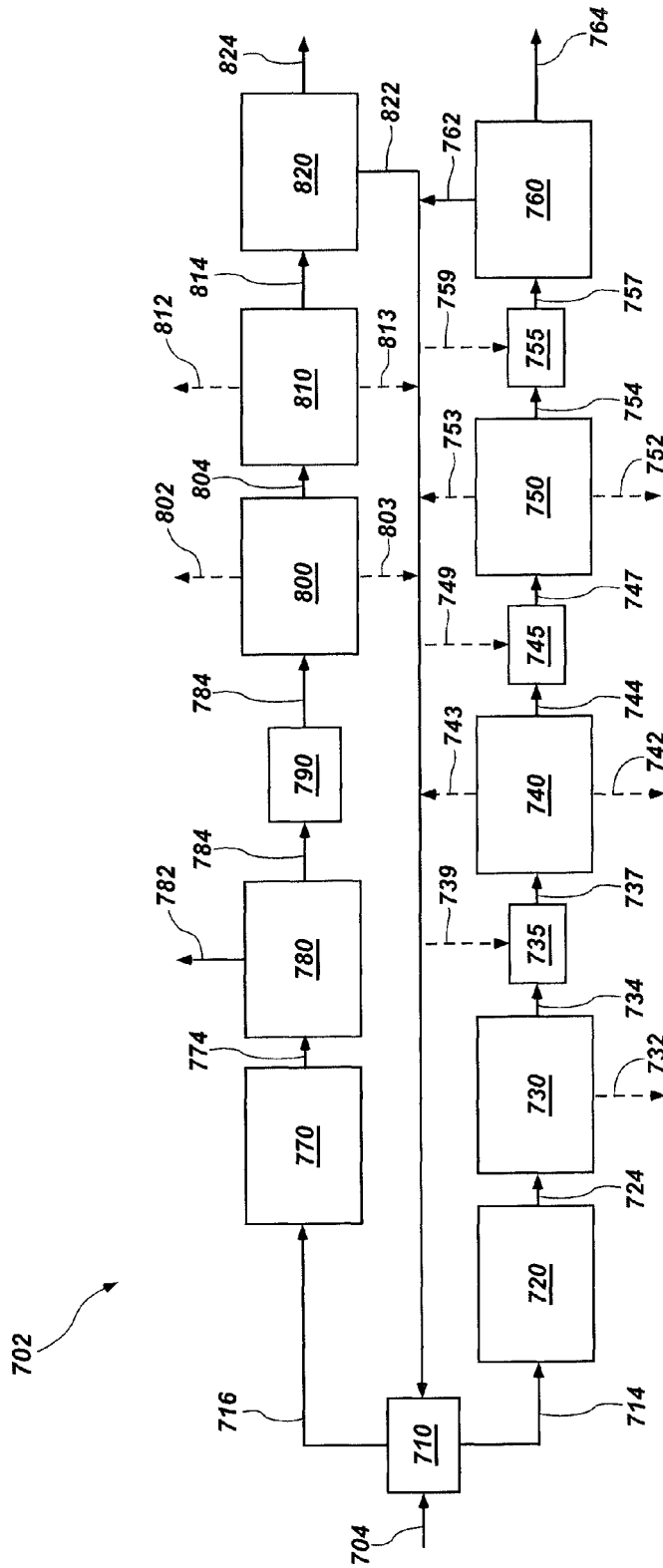
* cited by examiner

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6
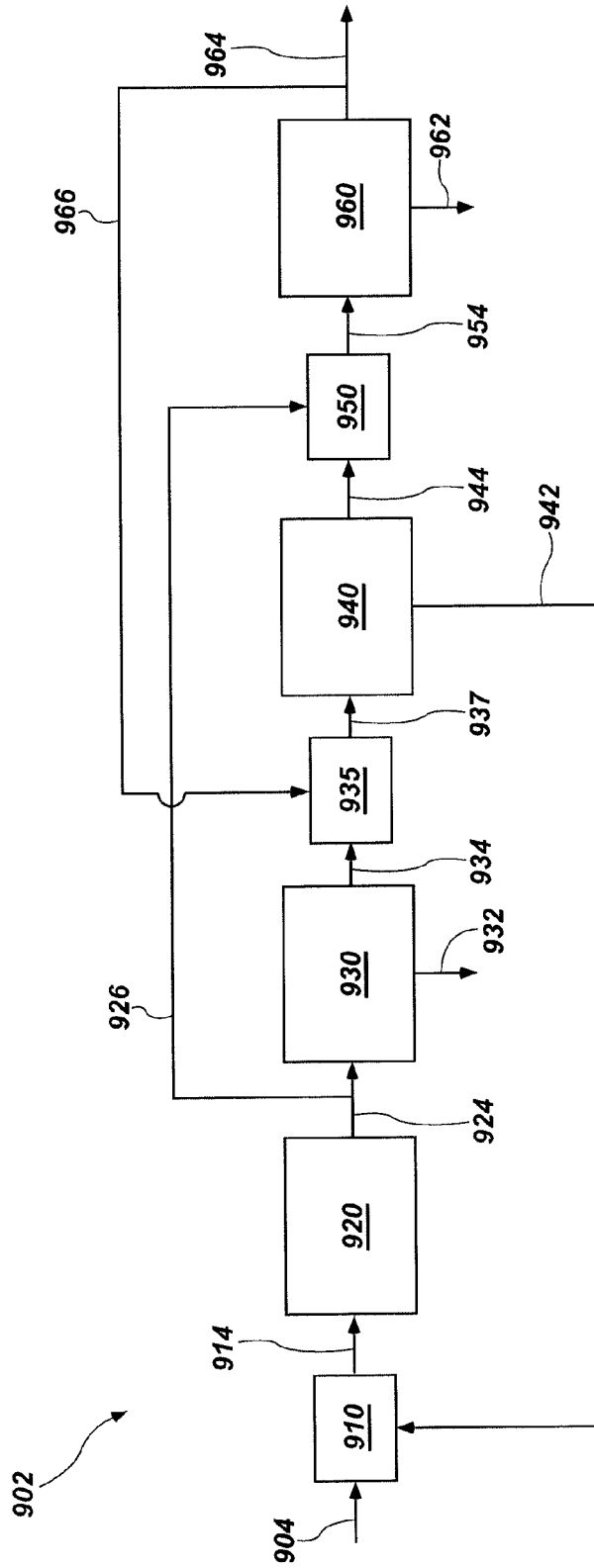
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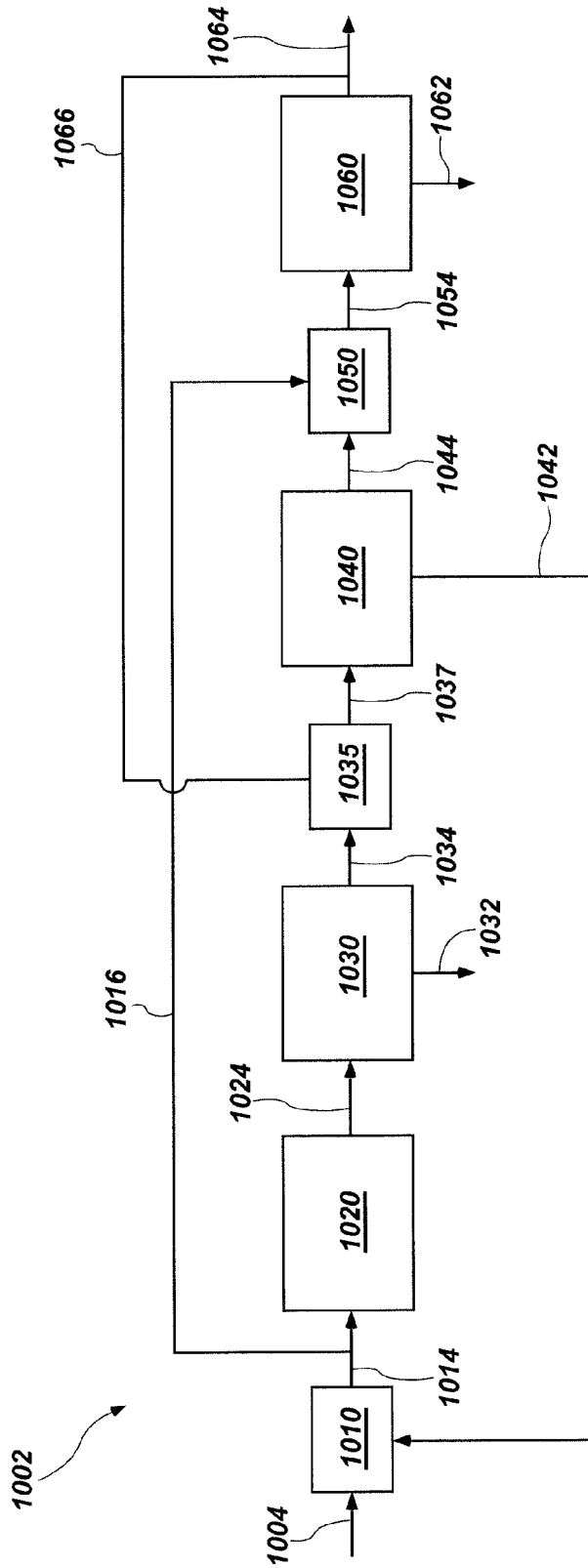
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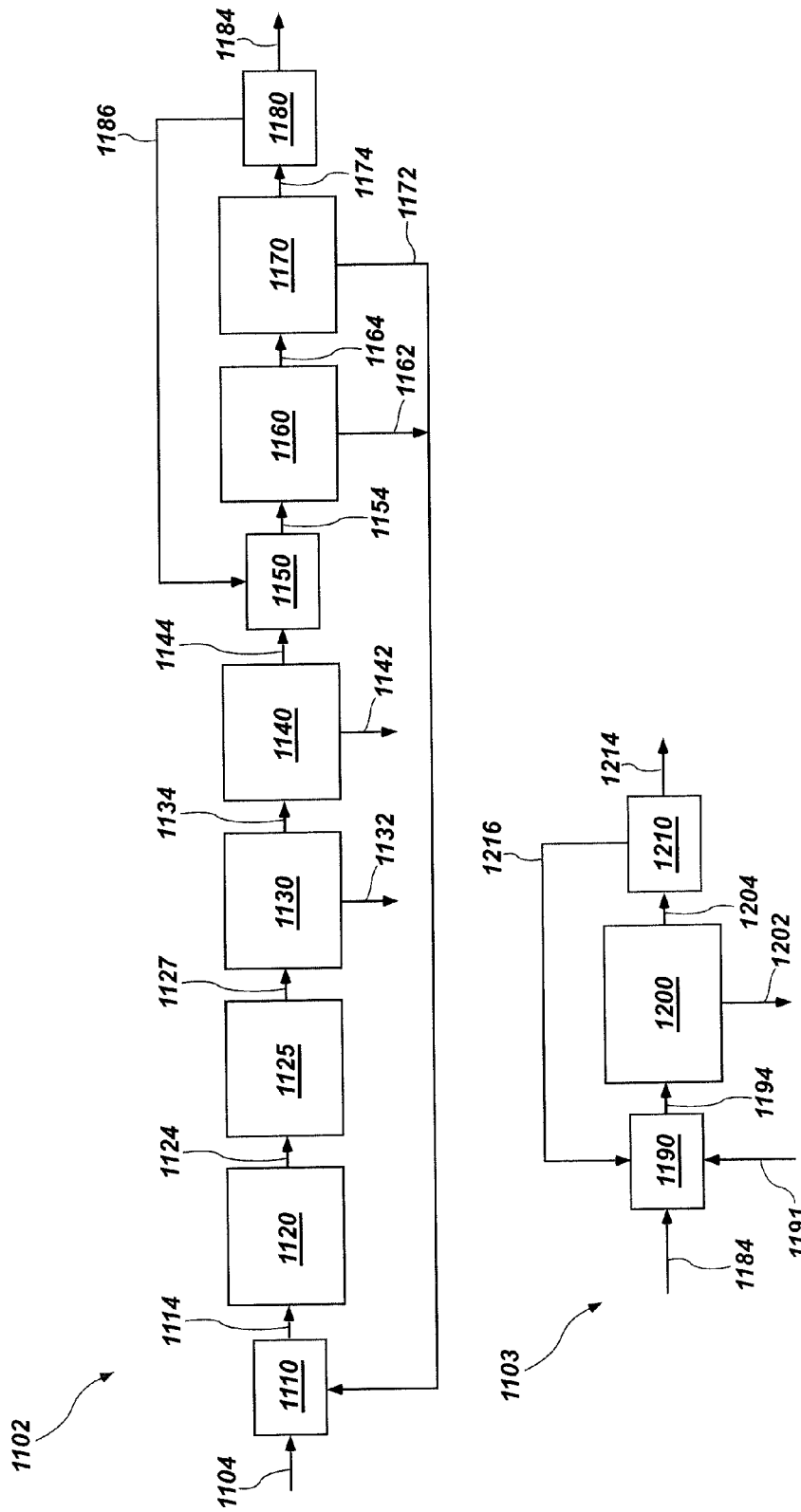
FIG. 9
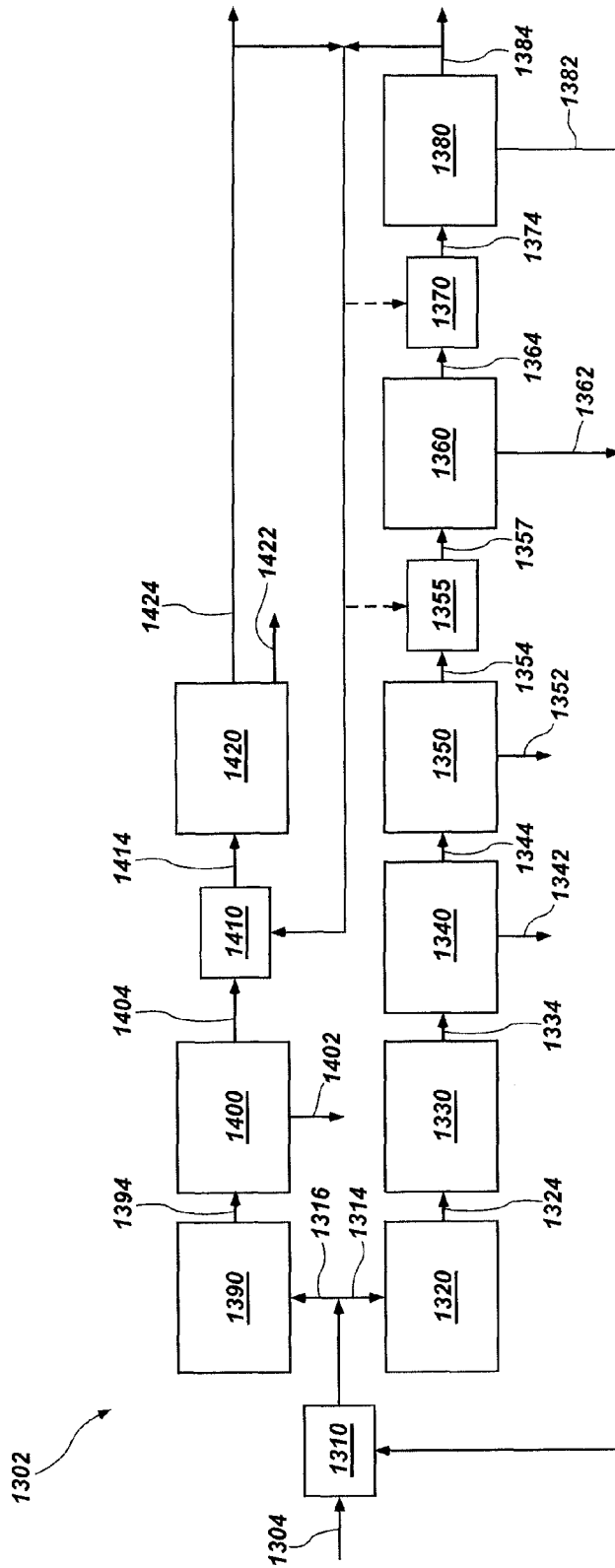
FIG. 10
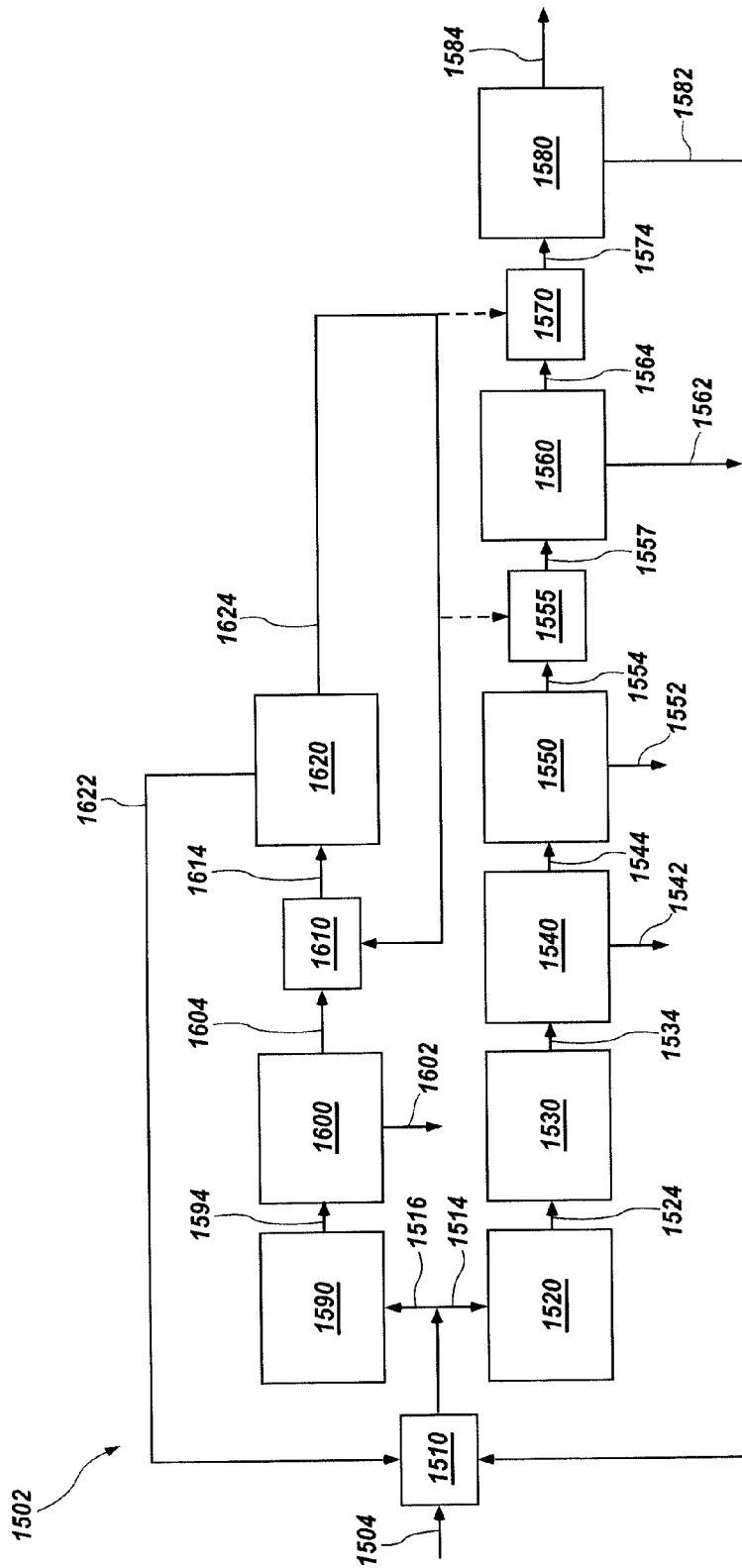
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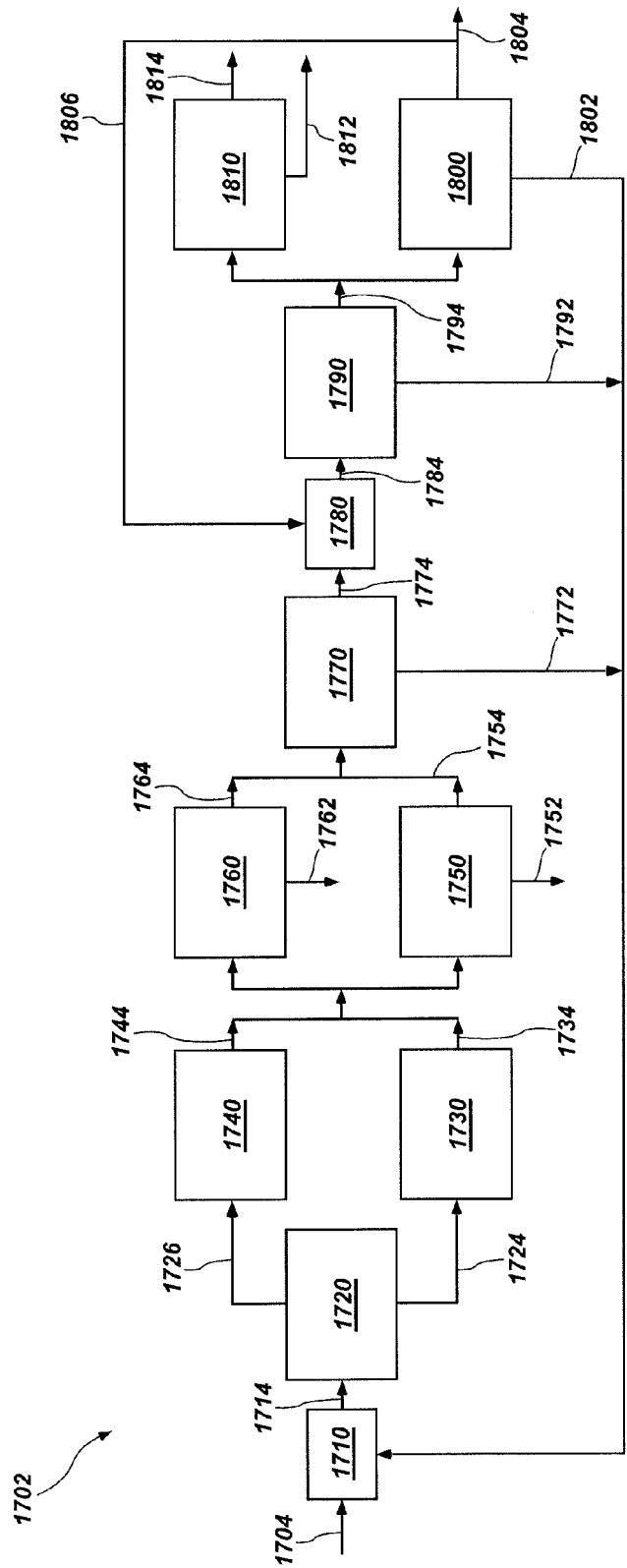
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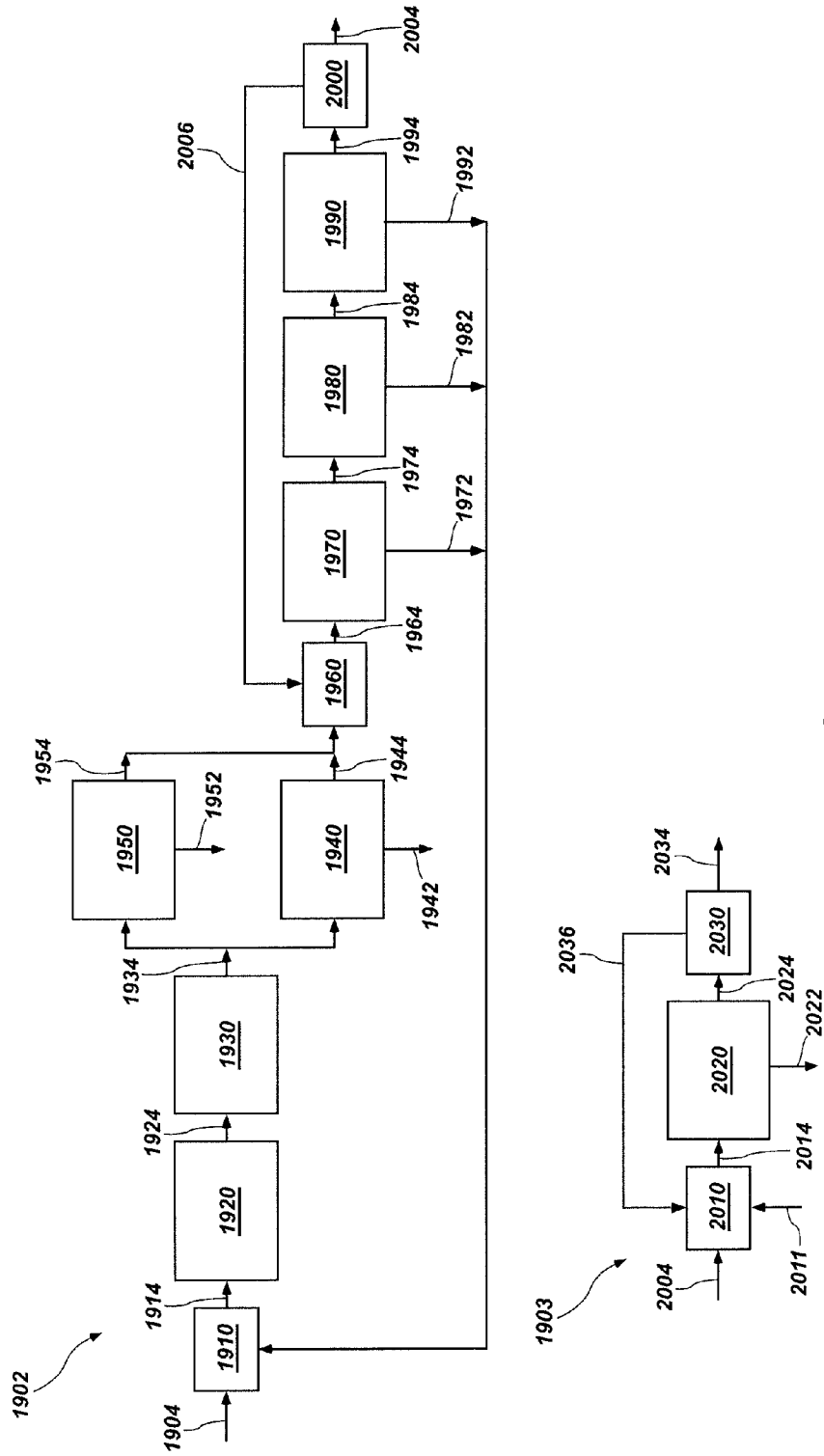
FIG. 13

METHODS OF PROCESSING SOLUTIONS OF POTASSIUM SULFATE AND MAGNESIUM SULFATE, METHODS OF PRODUCING POTASSIUM SULFATE, AND RELATED SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 14/023,347, filed Sep. 10, 2013, now U.S. Pat. No. 8,802,048, issued Aug. 12, 2014, which claims the benefit of U.S. Provisional Patent Application Ser. No. 61/699,917, filed Sep. 12, 2012, in the name of Chastain et al., the disclosure of each of which is hereby incorporated herein in its entirety by this reference.

FIELD

The present disclosure relates generally to processing aqueous solutions of alkali-metal and alkaline-earth-metal complexes to produce sulfate of potash, langbeinite, and/or other alkali-metal- and alkaline-earth-metal-containing products.

BACKGROUND

Polyhalite is a mineral having the formula $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$, which occurs naturally in, for example, deposits in Texas, New Mexico, Ukraine, and Germany. Ore deposits are conventionally sub-surface mined to produce ore in rock or chunk form because polyhalite is not sufficiently water-soluble to allow ore deposits to be economically solution-mined.

Polyhalite may be used in the production of various salts, such as potassium sulfate (also known as sulfate of potash or SOP), potassium magnesium sulfate, potassium calcium sulfate, potassium hydroxide, magnesium sulfate, etc. Some potassium salts are important ingredients in fertilizers and feedstocks for various industrial processes.

Polyhalite is soluble or leachable in aqueous solutions without calcining (i.e., heating to a temperature at which the polyhalite at least partially dissociates), but dissolution is relatively slow. Several methods of processing polyhalite ores are known, such as those described in John E. Conley and Everett P. Partridge, "Potash Salt from Texas-New Mexico Polyhalite Deposits: Commercial Possibilities, Proposed Technology, and Pertinent Salt-Solution Equilibria," U.S. Dept. of the Interior Bureau of Mines Bulletin 459 (1944), which is incorporated herein in its entirety by this reference. For example, polyhalite may be calcined by methods known in the art, and K_2SO_4 and $MgSO_4$ may be extracted by hot water, cold water, or other methods. The resulting liquor may be subjected to various processes in order to yield products such as potassium sulfate (SOP or K_2SO_4), leonite ($K_2SO_4MgSO_4 \cdot 4H_2O$), schoenite ($K_2SO_4MgSO_4 \cdot 6H_2O$), langbeinite ($K_2SO_4 \cdot 2MgSO_4$), kieserite ($MgSO_4 \cdot H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), etc.

Known methods of processing polyhalite ores generally require significant power and/or steam inputs, and may have process limitations. For example, in some processes, K_2SO_4 may be recovered with an efficiency of about 86%, but may not be in the form conventionally used as fertilizer (e.g., crystalline form, purity, etc.). In some processes, potassium may be produced entirely as SOP, but the efficiency may be only about 74%, and steam and power requirements may be relatively higher. In still other processes, K_2SO_4 efficiency

may be as high as 95%, but with higher steam and power requirements. Some processes may yield sulfate-containing products in less-than-ideal ratios (i.e., in ratios that do not maximize economic value of products). It would therefore be advantageous to provide a method of processing polyhalite that minimizes or alleviates these shortcomings.

BRIEF SUMMARY

In some embodiments, a method of processing an aqueous solution containing potassium sulfate and magnesium sulfate includes mixing recycle crystals with the aqueous solution, crystallizing potassium sulfate, and crystallizing the recycle crystals. The recycle crystals may include leonite and/or schoenite, and, optionally, potassium sulfate.

Other methods of processing a leach brine containing potassium sulfate and magnesium sulfate include mixing recycle crystals with the leach brine, crystallizing potassium sulfate from the concentrated solution to form a first potassium-depleted liquor, crystallizing the recycle crystals from the first potassium-depleted liquor to form a second potassium-depleted liquor, and crystallizing langbeinite from the second potassium-depleted liquor. The recycle crystals can be leonite or a mixture of leonite, schoenite, and optionally, potassium sulfate. Recycle crystals may also include other materials, such as calcium-containing salts.

Some systems for processing potassium sulfate and magnesium sulfate brines disclosed herein include a first crystallizer and a second crystallizer in fluid communication with the first crystallizer. The first crystallizer is structured and adapted to precipitate potassium sulfate from a concentrated liquor. The second crystallizer is structured and adapted to precipitate recycle crystals from the concentrated liquor to form a potassium-depleted recycle brine. The recycle crystals precipitated in the second crystallizer have a composition suitable to be recycled to the first crystallizer to increase the production of SOP.

In some embodiments, a process for producing potassium sulfate from a raw polyhalite ore includes: calcining solid particles of polyhalite to convert at least a portion of the solid particles of polyhalite to a water-soluble composition of compounds containing Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-}; dissolving the water-soluble composition within a leaching circuit to form a solution, producing an extract liquor having a molar ratio of K_2SO_4 to $MgSO_4$ of about 1:1; adding recycle crystals comprising at least one of leonite and potassium sulfate to the extract liquor to produce an intermediate solution having a higher concentration of K_2SO_4 and $MgSO_4$ than the extract liquor; evaporating water from the concentrated solution under conditions adapted to produce a first evaporate solution having K_2SO_4 and $MgSO_4$ concentrations higher than the concentrated solution and to precipitate a calcium-containing salt therefrom in a first evaporation step; separating the calcium-containing salt from the first evaporate solution to produce an ultra-concentrated filtrate solution comprising K_2SO_4 and $MgSO_4$ having a higher concentration of these ions than the concentrated solution; evaporating sufficient water from the ultra-concentrated solution to produce crystals of potassium sulfate and a second evaporate solution in a second evaporation step; separating the crystals of potassium sulfate from the second evaporate solution to provide a potassium-sulfate product; evaporating sufficient water from the second evaporate solution to produce crystals including at least one of leonite and K_2SO_4 and a third evaporate solution in a third evaporation step; and recycling the crystals of leo-

nite or leonite and K_2SO_4 to the second evaporation step. Recycle crystals may also include other materials, such as schoenite.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1** through **13** are simplified block flow diagrams illustrating embodiments of systems and processes for producing SOP, recycle crystals, and langbeinite from an aqueous solution comprising potassium sulfate and magnesium sulfate.

DETAILED DESCRIPTION

Novel systems and processes for processing aqueous media derived from a naturally occurring ore comprising potassium sulfate and magnesium sulfate in various combinations and concentrations are described herein. The processes may include, for example, steps for concentration, crystallization, and physical separation (e.g., decantation, filtration, etc.), as described in further detail below. The processes generally include crystallization of various types of solutions to recover SOP, leonite and/or schoenite in a selective manner, and optionally, recovery of langbeinite. Some materials are recycled in certain processes to enhance product recovery, provide energy efficiencies, etc. Some processes include parallel operations to improve process flexibility, stability, or economics. Illustrations presented herein are representations employed to describe embodiments of the present disclosure.

As used herein, particular mineral names (e.g., polyhalite, leonite, langbeinite, etc.) may refer to as-mined minerals, minerals physically or chemically separated from as-mined minerals, or crystallized solids formed (e.g., crystallized) in industrial processes. Particular minerals described herein may be substantially pure or may be mixed with other materials or contaminants.

As used herein, the terms "multiple-effect evaporator" and "MEE" each mean and include a series or plurality of vessels (or "effects") operable to boil a portion of a liquid at elevated pressure, ambient pressure, or reduced pressure (vacuum). Heat extracted from one vessel may be transferred to another vessel. Multiple-effect evaporators are described in, for example, U.S. Pat. No. 2,769,489, issued Nov. 6, 1956, and entitled "Multiple Effect Evaporator," the disclosure of which is incorporated herein in its entirety by this reference.

As used herein, the terms "mechanical vapor recompression evaporator" and "MVR evaporator" each mean and include a vessel coupled to a blower or compressor operable to compress vapor from the vessel. The blower or compressor operates as the energy input to boil a portion of a liquid in the vessel. Mechanical vapor recompression evaporators are described in, for example, U.S. Pat. No. 4,303,468, issued Dec. 1, 1981, and entitled "Mechanical Vapor Recompression Evaporators," and U.S. Pat. No. 3,396,086, issued Aug. 6, 1968, and entitled "Recompression Evaporators," the disclosure of each of which is incorporated herein in its entirety by this reference. MVR evaporators may be powered by a variable-frequency drive, which may allow operation over a wide power range.

A system for processing an aqueous medium comprising potassium sulfate and magnesium sulfate (system **2**) is shown schematically in FIG. **1**. To simplify the figures and clarify the present disclosure, not every element or component of system **2** is shown or described herein. System **2** may also include appropriate piping, connectors, sensors, controllers, etc., as will be understood by those of ordinary skill in the art. System

2, as illustrated, includes a first mixing apparatus **10** for mixing a leach brine **4** with a recycle stream **42**. This leach brine **4** includes an aqueous medium containing dissolved and/or suspended species extracted from polyhalite ore. The recycle stream **42** typically includes predominantly solid potassium sulfate and magnesium sulfate. For example, the recycle stream **42** generally has a molar ratio of potassium sulfate to magnesium sulfate of at least about 1:1, such as up to about 1.6:1. The recycle stream **42** typically includes leonite and/or schoenite crystals, and may also include SOP. The recycle stream **42** formed within system **2** is described in further detail below. The leach brine **4** may be mixed with the recycle stream **42** to form a concentrated brine **14** that is more concentrated in potassium and magnesium than the leach brine **4**. The concentrated leach brine **14** may optionally include small amounts of undissolved solids.

The leach brine **4** may be formed, for example, as described in U.S. Patent Application Publication No. 2013/0121900, published May 16, 2013, and entitled "Methods of Processing Polyhalite Ore, Methods of Producing Potassium Sulfate, and Related Systems," the disclosure of which is incorporated herein in its entirety by this reference. For example, a polyhalite ore is crushed, washed, and calcined. Calcination is described in John E. Conley and Everett P. Partridge, "Potash Salt from Texas-New Mexico Polyhalite Deposits: Commercial Possibilities, Proposed Technology, and Pertinent Salt-Solution Equilibria," U.S. Dept. of the Interior Bureau of Mines Bulletin 459 (1944), previously incorporated by reference. Potassium and magnesium salts, when leached from the calcined polyhalite, form the leach brine **4**. Additional potassium-containing compounds may optionally be added to the leach brine **4** to increase recovery of potassium as SOP, as described herein. Some impurities from the polyhalite ore may be removed from the leach brine **4** before the leach brine **4** enters the system **2**. For example, calcium sulfate or other impurities may be removed to prevent crystallization of these salts and fouling of the system **2**. In some embodiments, some impurities that could be removed are allowed to remain in the leach brine **4** for economic or other reasons. For example, product specifications may allow some impurities to remain in an end product, and removal of those impurities may not increase the value of the end product.

In some embodiments, solid particles of polyhalite calcined for a sufficient period of time to convert at least partially to a water-soluble composition of Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} may be leached in an aqueous medium to form an extract liquor having a molar ratio of K_2SO_4 to $MgSO_4$ of about 1:1. Recycle crystals produced later in the process are introduced to the extract liquor to produce a more concentrated solution comprising K_2SO_4 and $MgSO_4$. Water evaporated from the concentrated solution under appropriate conditions produces an evaporate solution having K_2SO_4 and $MgSO_4$ concentrations higher than the feed solution and eventually precipitates SOP (K_2SO_4) in a crystallization step.

The first mixing apparatus **10**, when held at a temperature from about 70° C. to about 130° C., promotes the dissolution of recycle crystals. For example, the first mixing apparatus **10** may operate at a temperature of about 80° C. Increasing the concentration of the concentrated brine **14** by adding the recycle stream **42** may increase the production rate of valuable products, such as SOP.

The concentrated brine **14** may optionally enter an evaporator (not shown in FIG. **1**) to further increase the concentration of potassium, magnesium, and sulfate ions. Such an evaporator may be, for example, a mechanical vapor recompression (MVR) evaporator operable to remove from about 10 wt % to about 50 wt %, from about 20 wt % to about 40 wt

%, or from about 25 wt % to about 35 wt % of the water from the concentrated brine 14. In a typical operation, the evaporator removes about 30 wt % of the water from the concentrated brine 14. The evaporator operates generally at temperatures from about 80° C. to about 110° C., such as from about 95° C. to about 100° C. The evaporator may be integral to a subsequent operation, such as an SOP crystallizer 20, described below.

The concentrated brine 14 enters the SOP crystallizer 20, which is operable to crystallize SOP 22 (i.e., K_2SO_4) from the concentrated brine 14. The SOP crystallizer 20 may include an MVR evaporator, an MEE, any combination thereof, or any other apparatus operable to promote crystallization of dissolved species. The SOP crystallizer 20 may operate, for example, at a temperature in a range from about 40° C. to about 100° C., such as in a range from about 70° C. to about 90° C. The SOP 22 produced is further processed by filtering, washing, drying, agglomerating (e.g., granulating or compacting) etc., as necessary to produce fertilizer-grade K_2SO_4, soluble-grade K_2SO_4, or another selected grade of K_2SO_4. Upon removal of the crystallized SOP 22, remaining liquor 24 is transferred to a second mixing apparatus 30, where the liquor 24 may optionally be mixed with a portion 56 of a potassium-depleted brine 44 to form an enriched liquor 34.

The enriched liquor 34 enters a recycle crystallizer 40 operable to form recycle crystals and produce recycle stream 42 from the enriched liquor 34, forming a potassium-depleted brine 44. The recycle crystallizer 40 may include an MVR evaporator, an MEE, any combination thereof, or any other apparatus operable to promote crystallization of dissolved species. In some embodiments, the recycle crystallizer 40 includes stages of an MEE, and the recycle crystallizer 40 may be a continuation of an MEE that includes the SOP crystallizer 20 (i.e., some stages of an MEE are included in the SOP crystallizer 20, and some are included in the recycle crystallizer 40). The recycle crystallizer 40 may operate, for example, at a temperature in a range from about 40° C. to about 80° C., such as in a range from about 50° C. to about 70° C.

The potassium-depleted brine 44 may be separated into two portions 54, 56 in a splitting device 50 (e.g., a valve, a tank, etc.). One portion 56, if split, recycles to the second mixing apparatus 30, as described above. Alternatively, the portion 56 may be recycled to another location, such as to the first mixing apparatus 10 or to a point within the recycle crystallizer 40 (e.g., between MEE stages). The other portion 54 enters a third mixing apparatus 60, where it mixes with SOP 62 to form a magnesium- and potassium-rich liquor 64. The SOP 62 may be a portion of the SOP 22 formed in the SOP crystallizer 20, or may be SOP from another source. In some embodiments, the SOP 62 may be a liquid, suspension, or hydrated form of K_2SO_4, or may include other materials.

The magnesium- and potassium-rich liquor 64 enters a langbeinite crystallizer 70 operable to crystallize langbeinite 72 from the magnesium- and potassium-rich liquor 64. A purge stream 74 removes uncrystallized ions from the system 2. Optionally, the langbeinite crystallizer 70 may be decoupled from the rest of the system 2 (e.g., from the SOP crystallizer 20, the recycle crystallizer 40, and the mixing apparatuses 10 and 30). Such decoupling allows the amount of langbeinite 72 produced to vary, such as to maximize economic output of the system 2, while maintaining many operating parameters. Since formation of langbeinite 72 decreases the amount of SOP 22 available for sale (i.e., because some SOP 62 is used as an input), market conditions may suggest making less langbeinite 72 than is theoretically possible. That is, the purge stream 74 may include a concen-

tration of magnesium ions that could be recovered, but that is profitably treated for disposal instead (e.g., because the SOP needed to convert the magnesium ions to langbeinite is more valuable than the langbeinite that could be produced). In some embodiments, the purge stream 74 is used to produce epsomite, kieserite, or some other material. In some embodiments, the third mixing apparatus 60 may be omitted or bypassed, and SOP 62 may not be added to the portion 54 of the potassium-depleted brine 44. In such embodiments, the portion 54 of the potassium-depleted brine 44 may form epsomite, kieserite, or some other material in the langbeinite crystallizer 70 (i.e., instead of or in addition to langbeinite). In some embodiments, a portion or all of the recycle stream 42 may be diverted for sale or use as a separate product. Such diversion would alter the product mix and/or the product yield, but may be beneficial under some economic conditions.

In some embodiments, other salts may be removed within the system 2. For example, calcium may be precipitated as calcium sulfate ($CaSO_4$) or as polyhalite before the first mixing apparatus 10, the SOP crystallizer 20, the second mixing apparatus 30, the recycle crystallizer 40, the third mixing apparatus 60, and/or the langbeinite crystallizer 70. The solubility of calcium sulfate in aqueous solutions decreases with increasing temperature, so calcium removal may limit or prevent problems associated with fouling (e.g., decreased efficiency, increased maintenance expenses, etc.). Calcium precipitates may be separated from other products, such as by differences in particle size or by density.

Another system 102 for processing an aqueous medium comprising potassium sulfate and magnesium sulfate is shown schematically in FIG. 2. System 102 includes a first mixing apparatus 110 for mixing a leach brine 104 with one or more recycle streams 132, 173. For example, the leach brine 104 may include an aqueous medium containing dissolved and/or suspended species extracted from polyhalite ore. The recycle streams 132, 173 include solid crystals primarily composed of potassium sulfate and magnesium sulfate (e.g., as leonite, schoenite, etc.), such as the recycle stream 42 described above. The leach brine 104 is mixed with the recycle streams 132, 173 to form concentrated brines 114, 116, which are more concentrated in potassium and magnesium than the leach brine 104. The concentrated leach brines 114, 116 may optionally include small amounts of undissolved solids.

The first mixing apparatus 110, when held at a temperature from about 70° C. to about 130° C., promotes the dissolution of recycle crystals. For example, the first mixing apparatus 110 may operate at a temperature of about 80° C. Increasing the concentration of the concentrated brine 114, 116 by adding the recycle streams 132, 173 may increase the production rate of valuable products, such as SOP.

The concentrated brine 114, 116 may enter one or more evaporators (not shown in FIG. 2) to further increase the concentration of potassium, magnesium, and sulfate ions. The evaporators may include, for example, a mechanical vapor recompression (MVR) evaporator operable to remove from about 10 wt % to about 50 wt %, from about 20 wt % to about 40 wt %, or from about 25 wt % to about 35 wt % of the water from the concentrated brine 114, 116. In some embodiments, the evaporators remove about 30 wt % of the water from the concentrated brine 114, 116. The evaporators may operate at temperatures from about 80° C. to about 110° C., such as from about 95° C. to about 100° C. The evaporators may be integral to subsequent operations, such as an SOP crystallizer (e.g., an evaporator may be part of the same vessel

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as an SOP crystallizer). If two or more evaporators are used, portions of each concentrated brine **114**, **116** may pass through parallel evaporators.

The concentrated brine **114**, **116** is split and processed in parallel in two or more processing operations **106**, **108**. In the first processing operation **106**, one portion of the concentrated brine **114** enters an SOP crystallizer **120**, which is operable to crystallize SOP **122** (i.e., K_2SO_4) from the concentrated brine **114**. The SOP crystallizer **120** may include an MVR evaporator, an MEE, any combination thereof, or any other apparatus operable to promote crystallization of dissolved species. The SOP crystallizer **120** may operate, for example, at a temperature in a range from about 40° C. to about 100° C., such as in a range from about 70° C. to about 90° C. The SOP **122** produced may be further processed, such as by filtering, washing, drying, agglomerating (e.g., granulating or compacting), etc.

Upon removal of the crystallized SOP **122**, remaining liquor **124** is optionally transferred to a second mixing apparatus **125**, which may mix the liquor **124** with a portion **146** of potassium-depleted brine **134**, as described in further detail below. The resulting liquor **127** is transferred to a recycle crystallizer **130** operable to form recycle stream **132** (which may include, for example, leonite, schoenite, and optionally SOP) from the liquor **124**, forming a potassium-depleted brine **134**. The recycle crystallizer **130** may include an MVR evaporator, an MEE, any combination thereof, or any other apparatus operable to promote crystallization of dissolved species. In some embodiments, the recycle crystallizer **130** includes stages of an MEE, and the recycle crystallizer **130** is a continuation of the MEE (i.e., some stages of the MEE are included in the SOP crystallizer **120**, and some are included in the recycle crystallizer **130**, which may or may not be a separate vessel). The recycle crystallizer **130** may operate, for example, at a temperature in a range from about 40° C. to about 80° C., such as in a range from about 50° C. to about 70° C. Alternatively, the recycle stream **132** may be recycled to another location, such as to the second mixing apparatus **125** or to a point within the recycle crystallizer **130** (e.g., between MEE stages).

The potassium-depleted brine **134** may be separated into two or more portions **144**, **146** in a splitting device **140** (e.g., a valve, a tank, etc.). One portion **144**, if split, may be purged from the system **102**. Another portion **146** is transferred to the second processing operation **108** and/or to the second mixing apparatus **125**. The recycle of the portion **146** of the potassium-depleted brine **134** may alter the composition of intermediate liquors, enabling precipitation of different species.

In the second processing operation **108**, the second portion of the concentrated brine **116** enters an SOP crystallizer **150** operable to crystallize SOP **152** (i.e., K_2SO_4) from the concentrated brine **116**, leaving a liquor **154**. The SOP crystallizer **150** may include an MVR evaporator, an MEE, any combination thereof, or any other apparatus operable to promote crystallization of dissolved species. The SOP crystallizer **150** may operate, for example, at a temperature in a range from about 40° C. to about 100° C., such as in a range from about 70° C. to about 90° C. The SOP **152** produced may be further processed, such as by filtering, washing, drying, agglomerating (e.g., granulating or compacting), etc.

Upon removal of the crystallized SOP **152**, the liquor **154** may optionally be mixed with the portion **146** of potassium-depleted brine **134** in a third mixing apparatus **160** to form a liquor **164**. The liquor **164** may enter a crystallizer **170** operable to crystallize SOP **172** and/or recycle stream **173** from the liquor **164**. Whether SOP **172** or recycle stream **173** or both are formed depends on the operating conditions of the

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crystallizer **170** and/or on the composition of the liquor **164**. For example, addition of the portion **146** of potassium-depleted brine **134** to the third mixing apparatus **160** causes an increase in the concentration of magnesium in the liquor **164**, such that leonite may be formed instead of SOP. If the portion **146** of potassium-depleted brine **134** is not added to the third mixing apparatus **160**, SOP **172** is formed in the crystallizer **170**. If SOP **172** is formed, the SOP **172** is removed for optional further processing, such as by filtering, washing, drying, granulating, etc. If leonite is formed in the crystallizer **170**, the leonite is typically recycled to the first mixing apparatus **110** via recycle stream **173**. A liquor **174** leaving the crystallizer **170** enters a langbeinite crystallizer **180** operable to crystallize langbeinite **182** from the liquor **174**. A purge stream **184** carries uncrystallized ions from the system **102**. Alternatively, the recycle stream **173** may be recycled to another location, such as to the third mixing apparatus **160** or to a point within the crystallizer **170** (e.g., between MEE stages).

In some embodiments, the potassium-depleted brine **134** from the first processing operation **106** may all be purged from the system **102**. In such embodiments, the portion **146** of potassium-depleted brine **134** is not transferred to the second processing operation **108** or to the second mixing apparatus **125** of the first processing operation **106**. Therefore, the second processing operation **108** may be configured to operate in a similar manner to the first processing operation **106**. The flow of the portion **146** of the potassium-depleted brine **134** may be varied during operation, such as to vary the quantity and composition of products. For example, the flow of the portion **146** of the potassium-depleted brine **134** to the third mixing apparatus **160** may be stopped to increase the production of SOP **122**, **152**, **172**, and the flow of the portion **146** of the potassium-depleted brine **134** may be started to produce langbeinite **182**. Thus, the product mix may be controlled during operation of the system **102**, such as to maximize economic value of the products.

In some embodiments, operation of the langbeinite crystallizer **180** is decoupled from the rest of the second processing operation **108** (e.g., from the SOP crystallizer **150**, the crystallizer **170**, and the third mixing apparatus **160**). Such decoupling allows the amount of langbeinite **182** produced to vary, such as to maximize economic output of the system **102**. Since formation of langbeinite **182** decreases the amount of SOP **172** available for sale, market conditions may suggest making less langbeinite **182** than is theoretically possible. That is, the purge stream **184** may include a concentration of magnesium ions that could be recovered, but that is profitably treated for disposal instead (e.g., because the SOP needed to convert the magnesium ions to langbeinite is more valuable than langbeinite that could be produced). In some embodiments, the purge stream **184** is used to produce epsomite, kieserite, or some other material.

Langbeinite may alternatively be formed at any selected point in the process. For example, langbeinite may be formed from the concentrated brine **114**, **116**, any of the liquors **124**, **127**, **154**, **164**, **174**, and/or the potassium-depleted brine **134**. Langbeinite may be used to form leonite or schoenite via decomposition, or may itself be a useful product. Alternatively, in some embodiments, leonite or schoenite may be formed directly from the concentrated brine **114**, **116**, any of the liquors **124**, **127**, **154**, **164**, **174**, and/or the potassium-depleted brine **134** without first forming langbeinite.

The first processing operation **106** and the second processing operation **108** may each be configured as MEEs or as MVR evaporators. MEEs and MVR evaporators may operate at temperature ranges from about 30° C. to about 115° C., for

example, from about 50° C. to about 100° C. MVR evaporators are generally designed to have a narrower operating range than MEEs, such as from about 85° C. to about 100° C. Operating ranges of equipment are selected based on economic and operational requirements.

The systems **2, 102** may include other elements or components not shown in FIG. **1** or **2**. For example, the systems **2, 102** may include material-handling equipment, such as pumps, augers, tilt tables, tanks, piping, sensors, valves, controllers, etc. The systems **2, 102** may be controlled by one or more computers, such as a programmable logic controller (PLC). In such embodiments, a computer detects operating conditions of the systems **2, 102** via one or more sensors and adjusts the flow of materials into, out of, or within the systems **2, 102** accordingly. The systems **2, 102** may alternatively or additionally be controlled by one or more human operators. Though shown as continuous-flow operations, the systems **2, 102** may also be configured to operate in batch mode, as will be understood by a person having ordinary skill in the art.

The processing methods and systems disclosed herein offer advantages over conventional methods and systems. For example, producing SOP as described herein may require less energy than conventional methods. Energy from one operation may be recovered for use in another operation described herein. Some systems of the present disclosure require smaller equipment, keeping capital and operating costs lower than in conventional processing systems, such as those requiring large evaporation ponds. In some embodiments, the ratio of products can be varied in-process, based on market demand or other factors. For example, a processing system **102** may operate such that all or nearly all of the potassium becomes SOP, while the magnesium is purged from the system for crystallization into epsomite, kieserite, etc. The same processing system may be operated at a different time with different operating conditions, such that as little as about 50% (on a molar basis) of the available potassium becomes SOP, while the remainder, along with magnesium, becomes langbeinite. The product mix may be shifted as necessary to maximize the value of products and to maximize profits. Such flexibility limits the economic risk of building a processing plant employing methods disclosed herein, because a decline in the price of one product may be at least partially offset by a change in the product mix.

The methods and systems disclosed herein may be used in conjunction with utilities (e.g., electricity, steam, etc.) supplied by local suppliers, and/or by cogeneration. For example, the systems **2, 102** may be designed such that a majority of the electricity required to operate is generated by one or more power-generation systems. Systems **2, 102** can be connected to a local electrical grid configured to continuously supply a small amount of electricity, and that can temporarily supply enough electricity to operate the system **2, 102** in the case of interruption of cogeneration. By sizing the cogeneration system to supply slightly less than the total operational needs, the cogeneration system continuously operates at full capacity without the need to sell excess power to local utility suppliers. Yet, the utility costs are controlled primarily by the costs of cogeneration fuel, rather than by electric utility rates. The system **2, 102** may also be configured to recover energy (e.g., as heat) from one portion of the process for use in another portion of the process.

A portion of the recovered products may be in an ultra-fine particle size. Such ultra-fine material may be advantageously granulated or pelletized to produce larger size particles, which are generally less prone to dusting, and are more easily handled.

Granulation, compaction, and/or pelletization may be accomplished in conventional equipment, such as a pan granulator, a pelletizer including one or more extruders, etc. Conventional organic and/or inorganic binding agents may be introduced to form granules or pellets having a selected size, hardness, purity, etc. For example, particles may be agglomerated with carbonates, sulfates, silicates, surfactants, fiber-based materials, polymers, starches, etc.

Granules or pellets may be formed by melting a small fraction of product (e.g., SOP or langbeinite) to form a free-flowing liquid, which may then be mixed with other particles in a granulator or pelletizer to form particles having a selected size, hardness, purity, etc. The melted material binds the particles together as it solidifies. Other inorganic chemicals may be melted for use as such a binder, and the binder may or may not have the same composition as the particles to be bound. Some possible binders include potassium sulfate, leonite, langbeinite, schoenite, magnesium carbonate, calcium sulfate, silicates, etc.

Granulation of products formed by processes disclosed herein may differ from granulation of natural mineral products (i.e., crystals produced from mining operations without recrystallization). For example, langbeinite formed by crystallization may incorporate water molecules in conventional granulation processes. Without being bound to any particular theory, it is believed that recrystallized langbeinite may partially decompose on contact with water. The water then becomes part of the crystalline structure by hydration. This hydration may contribute to formation of granules with desirable physical properties, but also decreases the weight fraction of potassium in the granules (generally expressed as K_2O content). To avoid this dilution of potassium content, it may be desirable to prevent or reverse water uptake by the crystalline structure.

In some embodiments, crystallized particles are partially dehydrated in one or more stages before granulation. For example, particles may be heated to a temperature of about 20° C. or higher, followed by a second heating to a temperature of about 90° C. or higher. In some embodiments, particles are dehydrated by heating to a temperature of at least 200° C. or at least 250° C. Granules may be dehydrated after the granulation process, in addition to or instead of dehydration before the granulation process. For example, granulated material may be heated to a temperature of about 100° C. or higher, or to a temperature of about 250° C. or higher. In certain embodiments, a shell is formed over granulated material. For example, water (e.g., a water mist, steam, etc.) added to a granulated material becomes incorporated into the crystalline structure of an outermost portion of the granulated material. Thus, a shell of hydrated crystalline material may surround or encapsulate an inner core.

In some embodiments, other products are recovered from various process flows. For example, a portion of leonite may be removed, filtered, dried, and granulated. As another example, some possible products include mixtures or solutions, such as soluble-grade fertilizers or products separable by flotation.

The following examples serve to explain embodiments of the present disclosure in more detail. These examples are not to be construed as being exhaustive or exclusive.

EXAMPLES

Example 1

Mechanical Vapor Recompression with Langbeinite Recycle

A process-flow diagram and system **302** for this example are shown in FIG. **3**. Leach brine **304** is mixed with recycle

crystals 362 in a mixer 310 to form liquor 314. Water is evaporated from liquor 314 in a pre-concentration evaporator 320 operating at about 100° C. to form liquor 324, which is more concentrated than liquor 314. Liquor 324 enters a first MVR evaporator 330 operating at about 85° C., wherein SOP crystals 332 are formed and removed to form liquor 334. Liquor 334 is mixed with potassium-depleted brine 364 in a mixer 340, forming liquor 344. Liquor 344 enters a second MVR apparatus 350 operating at about 100° C. Langbeinite crystals 352 form in the second MVR apparatus 350 and are separated from a purge stream 354. A portion 353 of the langbeinite crystals 352 is mixed with water 361 in a mixer 360 to form the recycle crystals 362 and the potassium-depleted brine 364. Another portion 355 of the langbeinite crystals 352 is removed from the system as a product. The recycle crystals 362 are recycled to the mixer 310, and the potassium-depleted brine 364 is recycled to the mixer 340.

Example 2

Mechanical Vapor Recompression without Langbeinite Recycle

A process-flow diagram and system 402 for this example are shown in FIG. 4. Leach brine 404 is mixed with recycle crystals 452 in a mixer 410 to form liquor 414. Water is evaporated from the liquor 414 in a pre-concentration evaporator 420 to form liquor 424. Liquor 424 enters a first MVR evaporator 430 operating at about 85° C., wherein SOP crystals 432 are formed and removed to form liquor 434. Liquor 434 is mixed with a portion 466 of potassium-depleted brine 454 in a mixer 440 to form liquor 444. Liquor 444 enters a second MVR evaporator 450 operating at about 70° C. The recycle crystals 452 form in the second MVR evaporator 450 and are separated from potassium-depleted brine 454. The crystals 452 are recycled back to the mixer 410. The potassium-depleted brine 454 is split in a splitting apparatus 460 to form two portions 464 and 466. One portion 466 is recycled to the mixer 440, and the other portion 464 enters a third MVR evaporator 470 operating at about 100° C. Langbeinite 472 is formed and separated from a purge stream 474 in the third MVR evaporator 470.

Example 3

Parallel Multiple-Effect Evaporation (MEE) to Form SOP and Langbeinite

A process-flow diagram and system 502 for this example are shown in FIG. 5. Leach brine 504 is mixed with recycle crystals 552, 562, 602 (which may include leonite and/or SOP) in a mixer 510 to form liquors 514, 516. Each liquor 514, 516 enters one of two MEEs. In one MEE shown in FIG. 5 (comprising pre-concentrators 520, 530 and crystallizers 540, 550, and 560), the first evaporation stage operates at about 100° C., and each subsequent stage operates at a temperature approximately 12° C. lower than the previous stage. Water is evaporated from liquor 514 in an MEE pre-concentrator 520 (i.e., an effect of an MEE) operating at about 100° C. to form liquor 524. Additional water is evaporated from liquor 524 in another MEE pre-concentrator 530 operating at about 88° C. to form liquor 534. Liquor 534 enters an SOP crystallizer 540 (i.e., a third MEE effect) operating at about 76° C. to form SOP crystals 542 and liquor 544. Liquor 544 optionally enters a mixer 545, where it may be mixed with a portion of a potassium-depleted stream 566 to form liquor 547. Liquor 547 enters a crystallizer 550 (i.e., a fourth MEE

effect) operating at about 64° C. to form recycle crystals 552 and liquor 554. Liquor 554 optionally enters a mixer 555, where it may be mixed with a potassium-depleted stream 566 to form liquor 557. Liquor 557 enters a crystallizer 560 (i.e., a fifth MEE effect) operating at about 50° C. to form recycle crystals 562 and liquor 564. SOP crystals 542 are separated for drying, granulation, and/or sale. SOP formed in the same stage as leonite (e.g., any SOP in the recycle crystals 552) is recycled to the mixer 510, with the leonite. The liquor 564 leaving the MEE is a potassium-depleted liquid that may be split between a purge stream 565 and a potassium-depleted stream 566 for input to a parallel process, as described below. Though two mixers 545 and 555 are shown in FIG. 5, the process may operate with only one mixer or without any mixers. In general, the mixer 545 or 555 (if present) is disposed before the first stage in which recycle crystals are formed.

Liquor 516 enters another MEE having four evaporation stages. Water is evaporated from liquor 516 in an MEE pre-concentrator 570 operating at about 100° C. to form liquor 574. Liquor 574 enters an SOP crystallizer 580 operating at about 76° C. to form SOP crystals 582 and liquor 584. Liquor 584 is mixed with a portion of the potassium-depleted stream 566, and, optionally, with potassium-depleted stream 615 in a mixer 590 to form liquor 594. Liquor 594 enters a crystallizer 600 operating at about 63° C. to form recycle crystals 602 and liquor 604. Liquor 604 enters a crystallizer 610 operating at about 88° C. to form langbeinite crystals 612 and liquor 614. SOP crystals 582 are separated for drying, granulation, and/or sale, and may be combined with SOP crystals 542 formed in the other MEE. SOP formed in the same stage as leonite (e.g., any SOP in the recycle crystals 602) is recycled to the mixer 510, with the leonite. Langbeinite crystals 612 are also separated for drying, granulation, and/or sale. The liquor 614 leaving the MEE is a potassium-depleted liquid that may be split between a purge stream 616 and the potassium-depleted stream 615 for recycle to mixer 590.

The volumetric flow through each MEE may be varied based on product demand. Thus, the product mix may be varied to maximize economic value.

Example 4

Parallel Multiple-Effect Evaporation (MEE) to Form SOP

A process-flow diagram and system 702 for this example are shown in FIG. 6. Example 4 is similar to Example 3, but without passing the potassium-depleted stream 566 to a parallel MEE process. The system 502 of FIG. 5 may be operated as described in Example 4, and the system 702 may be operated as described in Example 3, by redirecting the potassium-depleted stream 566 or the purge stream 764.

Leach brine 704 is mixed with recycle crystals 743, 753, 762, 803, 813, and/or 822 in a mixer 710 to form liquors 714, 716. Each liquor 714, 716 enters one of two MEEs. In one MEE shown in FIG. 6 (comprising effects 720, 730, 740, 750, and 760), the first effect 720 operates at about 100° C., and each subsequent effect operates at a temperature approximately 12° C. lower than the previous stage. Water is evaporated from liquor 714 in first effect 720 (a pre-concentrator) operating at about 100° C. to form liquor 724. Additional water may be evaporated from liquor 724 in second effect 730 (which may be another MEE pre-concentrator or an SOP crystallizer) operating at about 88° C. to form liquor 734. SOP 732 may optionally be formed in the second effect 730. Liquor 734 optionally enters a mixer 735, where it may be

mixed with a portion of recycle crystals **739** to form liquor **737**. Liquor **737** enters third effect **740** (a crystallizer) operating at about 76° C. to form SOP crystals **742** or recycle crystals **743** (e.g., leonite or leonite and SOP) and liquor **744**. If the third effect **740** forms essentially or entirely SOP crystals **742**, the SOP crystals **742** may be removed from the system **702** for further processing, sale, or use. If the third effect **740** forms leonite or leonite and SOP crystals, recycle crystals **743** may be recycled to a prior stage of the process. Liquor **744** optionally enters a mixer **745**, where it may be mixed with a portion of recycle crystals **749** to form liquor **747**. Liquor **747** enters a fourth effect **750** (a crystallizer) operating at about 64° C. to form SOP crystals **752** or recycle crystals **753** and liquor **754**, similar to those of the third effect **740**. If the fourth effect **750** forms leonite or leonite and SOP, these recycle crystals **753** may be recycled to a prior stage of the process. Liquor **754** optionally enters a mixer **755**, where it may be mixed with a portion of recycle crystals **759** to form liquor **757**. Liquor **757** enters a fifth effect **760** operating at about 50° C. to form recycle crystals **762** (e.g., leonite) and purge stream **764**. These recycle crystals **762** are also recycled to a prior stage of the process. The recycle crystals **743**, **753**, **762** may be recycled to the mixer **710**, the mixer **735**, the mixer **745**, and/or the mixer **755**. Though three mixers **735**, **745**, and **755** are shown between MEE effects in FIG. **6**, the process may operate with only one mixer or without any mixers. In general, the mixer **735**, **745**, or **755** (if present) is disposed before the first stage in which recycle crystals are formed.

Another MEE (comprising effects **770**, **780**, **800**, **810**, and **820**) operates in a similar manner. Water is evaporated from liquor **716** in first effect **770** (a pre-concentrator) operating at about 100° C. to form liquor **774**. SOP **782** is formed from liquor **774** in second effect **780** (a crystallizer) operating at about 88° C., and forming liquor **784**. Liquor **784** enters a mixer **790**, and leaves unchanged (the mixer **790** being reserved for operation in which a potassium-depleted stream is mixed). Liquor **784** enters third effect **800** (a crystallizer) operating at about 76° C. to form SOP crystals **802** or recycle crystals **803** and liquor **804**. If the third effect **800** forms essentially or entirely SOP crystals **802**, the SOP crystals **802** may be removed from the system **702** for further processing, sale, or use. If the third effect **800** forms recycle crystals **803**, the recycle crystals **803** may be recycled to the mixer **710**. Liquor **804** enters a fourth effect **810** (a crystallizer) operating at about 64° C. to form SOP crystals **812** or recycle crystals **813** and liquor **814**, similar to those of the third effect **800**. If the fourth effect **810** forms recycle crystals **813**, the recycle crystals **813** may be recycled to the mixer **710**. Liquor **814** enters a fifth effect **820** operating at about 50° C. to form leonite crystals **822** and purge stream **824**. The recycle crystals **822** are also recycled to the mixer **710**.

The product output of Examples 3 and 4 may be varied by switching the potassium-depleted recycle stream on or off. For example, when the only stream entering the mixer **790** is stream **784**, the third effect **800** and fourth effect **810** may produce SOP and/or leonite crystals. If a portion of the purge stream **764** containing a potassium-depleted liquor is instead transferred to the mixer **790**, the third effect **800** and fourth effect **810** may produce langbeinite, and the fifth effect **820** may be bypassed. The flow of potassium-depleted liquor to mixer **790** may be varied with time to form an economically advantageous amount of each product. For example, the system **702** may be operated to produce SOP and langbeinite for one week by flowing potassium-depleted liquor from stream **764** to mixer **790**, then operated to produce SOP as the only sulfate product for two weeks by not flowing any potassium-

depleted liquor from stream **764** to mixer **790**. Thus, the product mix may be varied, such as to maximize economic value.

Example 5

Multiple-Effect Evaporation (MEE) to Form SOP and Langbeinite

A process-flow diagram and system **902** for this example are shown in FIG. **7**. Leach brine **904** is mixed with recycle crystals **942** (e.g., leonite or leonite and SOP) in a mixer **910** to form liquor **914**. Liquor **914** enters an MEE having a series of evaporation stages (e.g., four effects). The first evaporation stage operates at about 100° C., and each subsequent stage operates at a temperature approximately 12° C. lower than the previous stage. Water is evaporated from liquor **914** in an MEE pre-concentrator **920** (a first effect of the MEE) operating at about 100° C. to form liquor **924**. A bypass portion **926** of the liquor **924** bypasses the next two effects, and the remainder of the liquor **924** enters an SOP crystallizer **930** (a second effect) operating at about 88° C. to form SOP crystals **932** and liquor **934**. Liquor **934** optionally enters a mixer **935**, where it may be mixed with a portion of a potassium-depleted stream **966** to form liquor **937**. Liquor **937** enters a crystallizer **940** (a third effect) operating at about 76° C. to form the recycle crystals **942** and liquor **944**. Liquor **944** is mixed with the bypass portion **926** of liquor **924** in mixer **950** to form liquor **954**. Liquor **954** enters a crystallizer **960** (a fourth effect) operating at about 62° C. to form langbeinite crystals **962** and purge stream **964**. SOP crystals **932** and langbeinite crystals **962** are separated for drying, granulation, and/or sale.

Example 6

Multiple-Effect Evaporation (MEE) to Form SOP and Langbeinite

A process-flow diagram and system **1002** for this example are shown in FIG. **8**. Example 6 is similar to Example 5, but with the bypass portion extracted before the first effect of the MEE.

Leach brine **1004** is mixed with recycle crystals **1042** in a mixer **1010** to form liquor **1014**. A bypass portion **1016** of the liquor **1014** bypasses the first three effects of an MEE having a series of evaporation stages (e.g., four effects), and the remainder of the liquor **1014** enters the MEE. The first stage operates at about 100° C., and each subsequent stage operates at a temperature approximately 12° C. lower than the previous stage. Water is evaporated from liquor **1014** in an MEE pre-concentrator **1020** (a first effect of the MEE) operating at about 100° C. to form liquor **1024**. Liquor **1024** enters an SOP crystallizer **1030** (a second effect) operating at about 88° C. to form SOP crystals **1032** and liquor **1034**. Liquor **1034** optionally enters a mixer **1035**, where it may be mixed with a portion of a potassium-depleted stream **1066** to form liquor **1037**. Liquor **1037** enters a crystallizer **1040** (a third effect) operating at about 76° C. to form recycle crystals **1042** and liquor **1044**. Liquor **1044** is mixed with the bypass portion **1016** of liquor **1014** in mixer **1050** to form liquor **1054**. Liquor **1054** enters a crystallizer **1060** (a fourth effect) operating at about 62° C. to form langbeinite crystals **1062** and purge stream **1064**. SOP crystals **1032** and langbeinite crystals **1062** are separated for drying, granulation, and/or sale.

Example 7

Multiple-Effect Evaporation (MEE) with Separate Langbeinite Crystallization

A process-flow diagram and systems **1102** and **1103** for this example are shown in FIG. **9**. Approximately 1654 tons per hour (TPH) of leach brine **1104** is mixed with approximately 301.4 TPH recycle crystals **1162**, **1172** in a mixer **1110** to form approximately 1955 TPH of liquor **1114**. The leach brine **1104** includes about 6.50 g K_2SO_4 per 100 g H_2O (about 6.71 moles of potassium sulfate per 1,000 moles of water) and about 4.49 g $MgSO_4$ per 100 g H_2O (about 6.71 moles of magnesium sulfate per 1,000 moles of water). The recycle crystals **1162**, **1172** include about 143.1 TPH of K_2SO_4, about 98.88 TPH of $MgSO_4$, and about 59.13 TPH of water. Water is evaporated from the liquor **1114** in a pre-concentration evaporator **1120** (a first effect of the MEE) operating at about 116° C. to form liquor **1124**. Liquor **1124** enters a second pre-concentration evaporator **1125** (a second effect of the MEE) operating at about 103° C. to form liquor **1127**. The pre-concentration evaporators **1120**, **1125** together evaporate approximately 366.2 TPH of water. The compositions of the materials entering and leaving the mixer **1110** and the pre-concentration evaporators **1120**, **1125** are as shown in Table 1 below.

TABLE 1

	Leach brine 1104	Recycle Crystals 1162 & 1172	Liquor 1114	Liquor 1127
g K_2SO_4 per 100 g H_2O	6.50	—	15.49	20.29
g $MgSO_4$ per 100 g H_2O	4.49	—	10.70	14.01
TPH K_2SO_4	96.85	143.1	240.0	240.0
TPH $MgSO_4$	66.90	98.88	165.8	165.8
TPH H_2O	1490	59.13	1549	1183
TPH total	1654	301.1	1955	1589

Liquor **1127** enters a crystallizer **1130** (a third effect) operating at about 89° C., wherein SOP crystals **1132** are formed and removed to form liquor **1134**. Liquor **1134** enters a crystallizer **1140** (a fourth effect) operating at about 75° C., wherein SOP crystals **1142** are formed and removed to form liquor **1144**. Together, the crystallizers **1130**, **1140** evaporate about 513.2 TPH of water to form about 87.56 TPH of SOP crystals **1132**, **1142** (which equals approximately 90.4% of the K_2SO_4 in the leach brine **1104**). Liquor **1144** is mixed with a potassium-depleted portion **1186** of liquor **1174** (which is potassium-depleted) in a mixer **1150** to form liquor **1154**. The compositions of the materials entering and leaving the crystallizers **1130**, **1140** and the mixer **1150** are as shown in Table 2 below.

TABLE 2

	Liquor 1127	Liquor 1144	Portion 1186 of Liquor 1174	Liquor 1154
g K_2SO_4 per 100 g H_2O	20.29	22.76	6.78	21.01
g $MgSO_4$ per 100 g H_2O	14.01	24.75	48.83	27.38
TPH K_2SO_4	240.0	152.4	5.57	158.0
TPH $MgSO_4$	165.8	165.8	40.14	205.9
TPH H_2O	1183	669.8	82.21	752.1
TPH total	1589	988.0	127.9	1116

Liquor **1154** enters a crystallizer **1160** (a fifth effect) operating at about 61° C., wherein recycle crystals **1162** are formed and removed to form liquor **1164**. Liquor **1164** enters a crystallizer **1170** (a sixth effect) operating at about 49° C., wherein recycle crystals **1172** are formed and removed to form liquor **1174**. A splitter **1180** divides the liquor **1174** into portions **1184**, **1186**, and portion **1184** is removed from the system **1102** to system **1103** for langbeinite production. Portion **1186** is recycled to the mixer **1150**. The crystallizers **1160** and **1170** together form a recycle crystallizer system, removing approximately 473.7 TPH of water and forming approximately 301.1 TPH of recycle crystals **1162** and **1172** as leonite. The compositions of the materials entering and leaving the recycle crystallizer system are as shown in Table 3 below.

TABLE 3

	Liquor 1154	Recycle Crystals 1162 & 1172	Liquor 1174	Portion 1184 of Liquor 1174	Portion 1186 of Liquor 1174
g K_2SO_4 per 100 g H_2O	21.01	—	6.78	6.78	6.78
g $MgSO_4$ per 100 g H_2O	27.38	—	48.83	48.83	48.83
TPH K_2SO_4	158.0	143.1	14.86	9.29	5.57
TPH $MgSO_4$	205.9	98.88	107.0	66.90	40.14
TPH H_2O	752.1	59.13	219.2	137.01	82.21
TPH total	1116	301.1	341.1	213.2	127.9

Langbeinite is formed in a separate system **1103**, decoupled from the MEE of system **1102**. Portion **1184** of liquor **1174** is mixed with approximately 11.27 TPH of SOP **1191** and approximately 85.14 TPH of a recycle stream **1216** in a mixer **1190** to form approximately 309.6 TPH of liquor **1194**. SOP **1191** may be a portion of SOP crystals **1132**, **1142** formed in the system **1102** described above or may be formed in some other process. Liquor **1194** enters a crystallizer **1200**, which may be an evaporator (e.g., single-effect evaporator, MEE, MVR evaporator, etc.) configured to remove approximately 47.09 TPH of water, forming approximately 35.49 TPH of langbeinite **1202** and approximately 227.0 TPH of liquor **1204**. The crystallizer **1200** or a portion thereof operates at a temperature of about 100° C. The langbeinite **1202** may be separated from liquor **1204** for drying, granulation, and/or sale, and a splitter **1210** divides the liquor **1204** into a purge stream **1214** and the recycle stream **1216**. The recycle stream **1216** is recycled to the mixer **1190**. The compositions of the material flows within the system **1103** are as shown in Table 4 below.

TABLE 4

	Portion 1184 of Liquor 1174	Recycle stream 1216	Liquor 1194	Liquor 1204	Purge stream 1214
g K_2SO_4 per 100 g H_2O	6.78	6.29	12.55	5.81	5.81
g $MgSO_4$ per 100 g H_2O	48.83	51.50	49.58	52.17	52.17
TPH K_2SO_4	9.29	3.40	23.96	8.25	5.16
TPH $MgSO_4$	66.90	27.79	94.69	74.10	46.31
TPH H_2O	137.01	53.95	191.0	142.0	88.77
TPH total	213.2	84.14	309.6	224.4	140.2

Because approximately 11.27 TPH of SOP **1191** is used as an input to the system **1103** for langbeinite production, the net

production of SOP from the systems **1102**, **1103** is about 76.29 TPH, or about 78.8% of the K_2SO_4 in the leach brine **1104**. However, 35.49 TPH of langbeinite **1202** includes another 14.9 TPH of K_2SO_4, for a total K_2SO_4 recovery of about 91.19 TPH (about 94.2%). The langbeinite **1202** (**35.49** TPH) also includes about 20.59 TPH of $MgSO_4$, for a total $MgSO_4$ recovery of about 30.77%. The systems **1102**, **1103** remove approximately 1400 TPH of water by evaporation.

By decoupling langbeinite formation from SOP formation, operating conditions for SOP production may be held constant regardless of langbeinite requirements. Variation of langbeinite production may require adjustment to operating conditions of the separate langbeinite process and adjustment of the amount of SOP used as an input to the langbeinite process.

Example 8

Multiple-Effect Evaporation (MEE) in Parallel with Mechanical Vapor Recompression (MVR)

A process-flow diagram and system **1302** for this example are shown in FIG. **10**. Leach brine **1304** is mixed with recycle crystals **1362**, **1382** in a mixer **1310** to form liquors **1314**, **1316**. Each liquor **1314**, **1316** enters one of two pre-concentrators **1320**, **1390** operating at about 100° C. The pre-concentrators **1320**, **1390** may be, for example, MVR evaporators. Though shown as two pre-concentrators **1320**, **1390**, in some embodiments, the liquors **1314**, **1316** leaving the mixer **1310** enter a single pre-concentrator, and are split after leaving the pre-concentrator. Furthermore, each pre-concentrator **1320**, **1390** may include two or more individual units operable to remove water.

Liquor **1324** leaving the pre-concentrator **1320** enters an MEE (comprising pre-concentrator **1330** and crystallizers **1340**, **1350**, **1360**, and **1380**). The first evaporation stage operates at about 100° C., and each subsequent stage operates at a temperature approximately 12° C. lower than the previous stage. Water is evaporated from liquor **1324** in a pre-concentrator **1330** (i.e., an effect of the MEE) operating at about 100° C. to form liquor **1334**. Liquor **1334** enters an SOP crystallizer **1340** (i.e., a second MEE effect) operating at about 88° C. to form SOP crystals **1342** and liquor **1344**. Liquor **1344** enters a crystallizer **1350** (i.e., a third MEE effect) operating at about 76° C. to form SOP crystals **1352** and liquor **1354**. Liquor **1354** optionally enters a mixer **1355**, where it may be mixed with a portion of liquor **1384** and/or **1424** to form liquor **1357**. Liquor **1357** enters a crystallizer **1360** (i.e., a fourth MEE effect) operating at about 64° C. to form recycle crystals **1362** and liquor **1364**. The liquor **1364** is optionally mixed with a portion of liquor **1384** and/or **1424** in a mixer **1370** to form liquor **1374**. Liquor **1374** enters a crystallizer **1380** (i.e., a fifth MEE effect) operating at about 50° C. to form recycle crystals **1382** and liquor **1384**. SOP crystals **1342** and **1352** are separated for drying, granulation, and/or sale. The liquor **1384** (which may be potassium-depleted) leaving the MEE is recycled to the mixer **1370**, transferred to a parallel process, as described below, and/or purged from the system **1302**. Though two mixers **1355**, **1370** are shown between MEE effects in FIG. **10**, the process may operate with only one mixer or without any mixers. In general, the mixer **1355** or **1370** (if present) is disposed before the first stage in which recycle crystals are formed.

The parallel process includes MVR evaporators. Liquor **1394** leaving the pre-concentrator **1390** enters an SOP crystallizer **1400** (an MVR evaporator) operating at about 85° C. to form SOP crystals **1402** and liquor **1404**. Liquor **1404** is

mixed with a portion of liquor **1384** and/or **1424** in a mixer **1410** to form liquor **1414**. Liquor **1414** enters a crystallizer **1420** operating at about 100° C. to form langbeinite crystals **1422** and liquor **1424**. SOP crystals **1402** and langbeinite crystals **1422** are each separated for drying, granulation, and/or sale. SOP crystals **1402** may be combined with SOP crystals **1342** and/or **1352** formed in the MEE. The liquor **1424** leaving the crystallizer **1420** is recycled to the mixer **1410**, transferred to the MEE process via mixer **1370**, and/or purged from the system **1302**.

In some embodiments, the potassium-depleted liquor **1384** leaving the MEE is mixed with the liquor **1424** leaving the crystallizer **1420**. In other embodiments, the liquor **1384** or the liquor **1424** supply all of the recycle needs, and the other of liquors **1384** and **1424** is purged. In some embodiments, the MEE and the MVR each supply their own recycle needs. The quantities and compositions of each liquor **1384** and **1424** recycled affect the composition of liquors **1357**, **1374**, and **1414** by changing the input to the mixers **1355**, **1370**, and **1410**.

The volumetric flow through the MEE and the MVRs may be varied based on product demand. Thus, the product mix may be varied, such as to maximize economic value.

Example 9

Multiple-Effect Evaporation (MEE) in Parallel with Mechanical Vapor Recompression (MVR)

A process-flow diagram and system **1502** for this example are shown in FIG. **11**. Example 9 is similar to Example 8, but without the formation of langbeinite.

Leach brine **1504** is mixed with recycle crystals **1562**, **1582**, and/or **1622** in a mixer **1510** to form liquors **1514**, **1516**. Each liquor **1514**, **1516** enters one of two pre-concentrators **1520**, **1590** operating at about 100° C. The pre-concentrators **1520**, **1590** may be, for example, MVR evaporators. Though shown as two pre-concentrators **1520**, **1590**, in some embodiments, the liquors **1514**, **1516** leaving the mixer **1510** enter a single pre-concentrator, and split after leaving the pre-concentrator. Furthermore, each pre-concentrator **1520**, **1590** may include two or more individual units operable to remove water.

Liquor **1524** leaving the pre-concentrator **1520** enters an MEE (comprising pre-concentrator **1530** and crystallizers **1540**, **1550**, **1560**, and **1580**). The first evaporation stage operates at about 100° C., and each subsequent stage operates at a temperature approximately 12° C. lower than the previous stage. Water is evaporated from liquor **1524** in a pre-concentrator **1530** (i.e., an effect of the MEE) operating at about 100° C. to form liquor **1534**. Liquor **1534** enters an SOP crystallizer **1540** (i.e., a second MEE effect) operating at about 88° C. to form SOP crystals **1542** and liquor **1544**. Liquor **1544** enters a crystallizer **1550** (i.e., a third MEE effect) operating at about 76° C. to form SOP crystals **1552** and liquor **1554**. Liquor **1554** optionally enters a mixer **1555**, where it may be mixed with a portion of liquor **1624** to form liquor **1557**. Liquor **1557** enters a crystallizer **1560** (i.e., a fourth MEE effect) operating at about 64° C. to form recycle crystals **1562** and liquor **1564**. The liquor **1564** is optionally mixed with a portion of liquor **1624** in a mixer **1570** to form liquor **1574**. Liquor **1574** enters a crystallizer **1580** (i.e., a fifth MEE effect) operating at about 50° C. to form recycle crystals **1582** and liquor **1584**. SOP crystals **1542** and **1552** are separated for drying, granulation, and/or sale. The liquor **1584** (which may be potassium-depleted) leaving the MEE is purged from the system **1502**. Though two mixers **1555**, **1570** are shown

between MEE effects in FIG. **11**, the process may operate with only one mixer or without any mixers. In general, the mixer **1555** or **1570** (if present) is disposed before the first stage in which recycle crystals are formed.

The parallel process includes MVR evaporators. Liquor **1594** leaving the pre-concentrator **1590** enters an SOP crystallizer **1600** (an MVR evaporator) operating at about 85° C. to form SOP crystals **1602** and liquor **1604**. Liquor **1604** may be mixed with a portion of liquor **1624** in mixer **1610** to form liquor **1614**. Liquor **1614** enters a crystallizer **1620** operating at about 70° C. to form recycle crystals **1622** and liquor **1624**. SOP crystals **1602** are separated for drying, granulation, and/or sale, and may be combined with SOP crystals **1542** and/or **1552** formed in the MEE. The liquor **1624** leaving the crystallizer **1620** is recycled to the mixer **1610**, and/or transferred to the MEE process via mixer **1570**. The liquor **1584** purged from the MEE may be further processed and/or disposed of.

Example 10

Multiple-Effect Evaporation (MEE) Stages Optionally in Parallel with Mechanical Vapor Recompression (MVR) Stages

A process-flow diagram and system **1702** for this example are shown in FIG. **12**. Leach brine **1704** is mixed with recycle crystals **1772**, **1792**, and/or **1802** in a mixer **1710** to form liquor **1714**. The liquor **1714** enters a pre-concentrator **1720** (e.g., an MVR evaporator) operating at about 100° C. Though shown as one pre-concentrator **1720**, in some embodiments, the pre-concentrator **1720** may include two or more individual units operable in series or in parallel to remove water.

Liquor **1724** leaving the pre-concentrator **1720** enters a pre-concentrator **1730**, comprising the first evaporation stage of an MEE, operating at about 100° C. Liquor **1726** also leaves the pre-concentrator **1720**, and is split from liquor **1724** by a splitter (not shown). Liquor **1726** enters a pre-concentrator **1740**, comprising an MVR evaporator, operating at about 100° C. Liquors **1734** and **1744** form in the pre-concentrators **1730** and **1740**, respectively. Liquors **1734** and **1744** may have the same or different compositions. In some embodiments, the operating conditions of one or both pre-concentrators **1730** and **1740** may vary based on the volume, temperature, and/or composition of the leach brine **1704**. For example, the pre-concentrator **1730** may be operated at a constant flow, and the pre-concentrator **1740** may have a variable flow to accommodate changes in the flow of the leach brine **1704**.

Liquors **1734** and **1744** may be combined in a mixer (not shown) and/or split in a splitter (not shown) before entering crystallizers **1750** and **1760**. Crystallizer **1750** is a second MEE effect operating at about 88° C. to form SOP crystals **1752** and liquor **1754**. Crystallizer **1760** is an MVR evaporator operating at about 88° C. to form SOP crystals **1762** and liquor **1764**. Liquors **1754** and **1764** may have the same or different compositions. In some embodiments, the operating conditions of one or both crystallizers **1750** and **1760** vary based on the volume, temperature, and/or composition of the liquors **1734** and **1744**. For example, the crystallizer **1750** may be operated at a constant flow, and the crystallizer **1760** may have a variable flow to accommodate changes in the flow of the liquors **1734** and **1744**. In some embodiments, the liquor **1734** passes entirely to the crystallizer **1750**, and the liquor **1744** passes entirely to the crystallizer **1760**, without any mixing thereof.

Liquors **1754** and **1764** may be mixed in a mixer (not shown) before entering a crystallizer **1770** (i.e., a third MEE

effect). The crystallizer **1770** operates at about 76° C. to form recycle crystals **1772** and liquor **1774**. Liquor **1774** is mixed with a recycle liquor **1806** (e.g., a potassium-depleted liquid) in a mixer **1780** to form liquor **1784**. Liquor **1784** enters a crystallizer **1790** (i.e., a fourth MEE effect) operating at about 64° C. to form recycle crystals **1792** and liquor **1794**. The liquor **1794** is divided into two portions in a splitter (not shown) before entering each of crystallizers **1800** and **1810**.

Crystallizer **1800** is a fifth MEE effect operating at about 50° C. to form recycle crystals **1802** and liquor **1804**. The recycle liquor **1806** is separated from the liquor **1804** by a splitter (not shown). Crystallizer **1810** is an MVR evaporator operating at about 100° C. to form langbeinite crystals **1812** and liquor **1814**. In some embodiments, the operating conditions of one or both crystallizers **1800** and **1810** may vary based on the volume, temperature, and/or composition of the liquors **1754** and **1764**. For example, the crystallizer **1800** may be operated at a constant flow, and the crystallizer **1810** may have a variable flow to accommodate changes in the flow of the liquors **1754** and **1764**. In some embodiments, the flow through crystallizers **1800** and **1810** may vary based on market conditions (e.g., demand for SOP versus demand for langbeinite).

The product output of Example 10 may be varied, such as to maximize economic value, by varying the amount of the liquor entering each of the MEE stages and MVR evaporators, for stages in which the liquor is split. MVR evaporators may be powered by variable frequency drives, which allow a wide range of operation, such that MEE stages may operate under nearly constant conditions.

Example 11

Multiple-Effect Evaporation (MEE) in Parallel with Mechanical Vapor Recompression (MVR); Separate Langbeinite Crystallization

A process-flow diagram and system **1902** for this example are shown in FIG. **13**. Approximately 1654 tons per hour (TPH) of leach brine **1904** is mixed with approximately 379.6 TPH of leonite crystals **1972**, **1982**, and/or **1992** in a mixer **1910** to form approximately 2033 TPH of liquor **1914**. The leach brine **1904** includes about 6.50 g K_2SO_4 per 100 g H_2O (about 6.71 moles of potassium sulfate per 1,000 moles of water) and about 4.49 g $MgSO_4$ per 100 g H_2O (about 6.71 moles of magnesium sulfate per 1,000 moles of water). The leonite crystals **1972**, **1982**, and/or **1992** combined include about 180.4 TPH of K_2SO_4, about 124.6 TPH of $MgSO_4$, and about 74.53 TPH of water. Water is evaporated from the liquor **1914** in a pre-concentration evaporator **1920** (e.g., an MVR evaporator, an MEE stage, any combination thereof, etc.) operating at about 100° C. to form liquor **1924**. Liquor **1924** enters a second pre-concentration evaporator **1930** (e.g., an MVR evaporator, an MEE stage, any combination thereof, etc.) operating at about 100° C. to form liquor **1934**. The pre-concentration evaporators **1920**, **1930** can also be operated in series. Regardless of the configuration, one of the pre-concentration evaporators **1920**, **1930** is the first effect of an MEE. Together, the pre-concentration evaporators **1920**, **1930** evaporate approximately 428.2 TPH of water. The compositions of the materials entering and leaving the mixer **1910**, the pre-concentration evaporators **1920**, **1930** are as shown in Table 5 below.

TABLE 5

	Leach brine 1904	Crystals 1972, 1982, & 1992	Liquor 1914	Liquor 1934
g K_2SO_4 per 100 g H_2O	6.50	—	17.72	24.40
g $MgSO_4$ per 100 g H_2O	4.49	—	12.24	16.86
TPH K_2SO_4	96.85	180.44	277.3	277.3
TPH $MgSO_4$	66.90	124.64	191.5	191.5
TPH H_2O	1490	74.53	1565	1136
TPH total	1654	379.6	2033	1605

The pre-concentration evaporators **1920**, **1930** facilitate forming a liquor **1934** having a concentration that remains approximately constant with time. That is, if the composition of the leach brine **1904** changes with time, the operating parameters of the pre-concentration evaporator **1920** and the pre-concentrator **1930** (e.g., heating loads, temperatures, pressures, etc.) may be controlled to maintain the liquor **1934** at a constant composition (i.e., unchanging with respect to time). Thus, control of subsequent operations may be simplified.

Liquor **1934** is split into two or more streams in a splitter (not shown), each entering a crystallizer **1940** or **1950**, which operate in parallel, but can also be configured to operate in series. The crystallizer **1940** is a second effect of the MEE operating at about 85° C., wherein SOP crystals **1942** are formed and removed to form liquor **1944**. The crystallizer **1950** is an MVR evaporator operating at about 85° C., wherein SOP crystals **1952** are formed and removed to form liquor **1954**. Together, the crystallizers **1940**, **1950** evaporate about 382.8 TPH of water to form about 87.56 TPH of SOP crystals **1942**, **1952** (which equals approximately 90.4% of the K_2SO_4 in the leach brine **1904**). The SOP crystals **1942** and **1952** may be combined, washed, dried, granulated, and/or sold. Liquors **1944**, **1954** (totaling about 1135 TPH) are combined in a mixer **1960** with a portion **2006** (about 127.9 TPH) of liquor **1994** to form about 1263 TPH of liquor **1964**. The portion **2006** of liquor **1994** is potassium-depleted, increasing the relative concentration of magnesium with respect to potassium, such that the liquor **1964** is at a point on the phase diagram that results in crystallizing leonite in a subsequent crystallizer **1970**. The compositions of the materials entering and leaving the crystallizers **1940**, **1950** and the mixer **1960** are as shown in Table 6 below.

TABLE 6

	Liquor 1934	Total of Liquors 1944, 1954	Portion 2006 of Liquor 1994	Liquor 1964
g K_2SO_4 per 100 g H_2O	24.40	25.18	6.78	23.37
g $MgSO_4$ per 100 g H_2O	16.86	25.42	48.83	27.72
TPH K_2SO_4	277.3	189.7	5.57	195.3
TPH $MgSO_4$	191.5	191.5	40.14	231.7
TPH H_2O	1136	753.6	82.21	835.8
TPH total	1605	1135	127.9	1263

Liquor **1964** enters the crystallizer **1970** (a third effect) operating at about 74° C., wherein leonite crystals **1972** are formed and removed to form liquor **1974**. Liquor **1974** enters a crystallizer **1980** (a fourth effect) operating at about 62° C., wherein leonite crystals **1982** are formed and removed to form liquor **1984**. Liquor **1984** enters a crystallizer **1990** (a fifth effect) operating at about 50° C., wherein leonite crystals **1992** are formed and removed to form approximately 341.1

TPH of liquor **1994**. A splitter **2000** divides the liquor **1994** into portions **2004** (approximately 213.2 TPH) and **2006** (approximately 127.9 TPH), and portion **2004** is removed from the system **1902** to a system **1903** for langbeinite production. Portion **2006** is recycled to the mixer **1960**. The crystallizers **1970**, **1980**, and **1990** together form a recycle crystallizer system, removing approximately 542.0 TPH of water and forming approximately 379.6 TPH of leonite crystals **1972**, **1982**, and **1992**. The compositions of the materials entering and leaving the recycle crystallizer system are as shown in Table 7 below.

TABLE 7

	Liquor 1964	Crystals 1972, 1982, & 1992	Liquor 1994	Portion 2004 of Liquor 1994	Portion 2006 of Liquor 1994
g K_2SO_4 per 100 g H_2O	23.37	—	6.78	6.78	6.78
g $MgSO_4$ per 100 g H_2O	27.72	—	48.83	48.83	48.83
TPH K_2SO_4	195.3	180.4	14.86	9.29	5.57
TPH $MgSO_4$	231.7	124.6	107.0	66.90	40.14
TPH H_2O	835.8	74.53	219.2	137.01	82.21
TPH total	1263	379.6	341.1	213.2	127.9

The recycle crystallizer system produces an amount of leonite and/or schoenite crystals **1972**, **1982**, and **1992** sufficient to remove most of the potassium from the solution (e.g., at least 80%, at least 90% or at least 95% of the K_2SO_4 entering from the leach brine **1904**). Thus, the amount of potassium leaving in the portion **2004** of the liquor **1994** may be minimized.

Langbeinite is formed in a separate system **1903**, decoupled from the MEE of system **1902**. Portion **2004** (approximately 213.2 TPH) of liquor **1994** is mixed with approximately 10.77 TPH of SOP **2011** and approximately 84.15 TPH of a recycle stream **2036** in a mixer **2010** to form approximately 308.1 TPH of liquor **2014**. The amount of SOP **2011** added to the portion **2004** of liquor **1994** is based upon the targeted langbeinite production rate (e.g., magnesium and potassium may be present in a molar ratio greater than or equal to 2:1 in the liquor **2014**). Langbeinite is formed from the liquor **2014**. The SOP **2011** may be a portion of one or both of SOP crystals **1942** or **1952** formed in the system **1902** for producing SOP. Liquor **2014** enters a crystallizer **2020**, which may be an evaporator (e.g., single-effect evaporator, MEE, MVR evaporator, etc.) configured to remove approximately 48.24 TPH of water, forming approximately 35.49 TPH of langbeinite **2022** and approximately 224.4 TPH liquor **2024**. The crystallizer **2020**, or a portion thereof, operates at a temperature of about 85° C. The langbeinite **2022** is separated from liquor **2024** for drying, granulation, and/or sale, and a splitter **2030** divides the liquor **2024** into a purge stream **2034** (approximately 140.2 TPH) and the recycle stream **2036**. The recycle stream **2036** is recycled to the mixer **2010**. The purge stream **2034** is removed from the system **1903** for treatment or disposal (e.g., as tailings). The compositions of the material flows within the system **1903** are as shown in Table 8 below.

TABLE 8

	Portion 2004 of Liquor 1994	Recycle stream 2036	Liquor 2014	Liquor 2024	Purge stream 2034
g K_2SO_4 per 100 g H_2O	6.78	5.81	12.17	5.81	5.81
g $MgSO_4$ per 100 g H_2O	48.83	52.17	49.77	52.17	52.17
TPH K_2SO_4	9.29	3.09	23.15	8.25	5.16
TPH $MgSO_4$	66.90	27.79	94.69	74.10	46.31
TPH H_2O	137.01	53.26	190.3	142.0	88.77
TPH total	213.2	84.15	308.1	224.4	140.2

Since approximately 10.77 TPH of SOP **2011** is used as an input to the system **1903** for langbeinite production, the net production of SOP from the systems **1902**, **1903** is about 76.79 TPH, or about 79.3% of the K_2SO_4 in the leach brine **1904**. However, 35.49 TPH of langbeinite **2022** includes another 14.9 TPH of K_2SO_4, for a total K_2SO_4 recovery of about 91.69 TPH (about 94.67%). The langbeinite **2022** (35.49 TPH) also includes about 20.59 TPH of $MgSO_4$, for a total $MgSO_4$ recovery of about 30.77%. The systems **1902**, **1903** remove approximately 1401 TPH of water by evaporation.

In some embodiments, some or all of the portion **2004** of the liquor **1994** leaving the crystallizer **1990** is sent to tailings or used to form kieserite and/or epsomite. Additional crystallization may be necessary to form kieserite or epsomite (e.g., additional potassium may be removed from the portion **2004** of the liquor **1994** before forming kieserite or epsomite).

In other embodiments, the entire portion **2004** of the liquor **1994** leaving the crystallizer **1990** is processed in the system **1903** to increase SOP recovery. That is, the portion **2004** of the liquor **1994** has a slightly higher percentage of SOP than the liquor **2024** leaving the crystallizer **2020**.

Operating conditions for SOP production (i.e., in system **1902**) may be held constant regardless of langbeinite requirements. By making SOP and langbeinite separately, the production amounts of each may be varied with minimal impact to the production process (e.g., to temperatures, flow rates, power and heating loads, etc.). Variation of langbeinite production requires adjustment to operating conditions of the separate langbeinite process (i.e., in system **1903**) and adjustment of the amount of SOP used as an input to the langbeinite process.

One advantage of the embodiment of Example 11, as described above and shown in FIG. **13**, is that energy use may be balanced between steam and electricity. The energy may be balanced on a stand-alone basis, may be coupled with the energy demands for the rest of the on-site facilities, or may be varied based on production rates and product ratios. This allows co-generation to be a workable option for this processing scenario. In addition, this processing scenario allows for flexibility in processing langbeinite or other secondary products without influencing the evaporative loads or the operation of equipment related to the manufacture of SOP.

While the disclosure is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, the disclosure is not intended to be limited to the particular forms disclosed. Rather, the disclosure is to cover all modifications, equivalents, and alternatives falling within the scope of the disclosure as defined by the following appended claims and their legal equivalents. In addition, features from one embodiment may be combined with features of another embodiment while still being encompassed within the scope of the present dis-

closure as contemplated by the inventors. Further, embodiments of the present disclosure have utility in the processing of various materials.

What is claimed is:

1. A method of processing a leach brine comprising potassium sulfate and magnesium sulfate, the method comprising:
    mixing recycle crystals with the leach brine to form an intermediate solution, the intermediate solution having a higher concentration of potassium sulfate and magnesium sulfate than the leach brine;
    crystallizing K_2SO_4 from the intermediate solution to form a first potassium-depleted liquor;
    crystallizing the recycle crystals from the first potassium-depleted liquor to recover additional potassium and to form a second potassium-depleted liquor; and
    crystallizing langbeinite from the second potassium-depleted liquor.

2. The method of claim **1**, wherein crystallizing K_2SO_4 from the intermediate solution comprises:
    dividing the intermediate solution into a plurality of portions; and
    separately crystallizing K_2SO_4 from each of the plurality of portions.

3. The method of claim **1**, further comprising removing water from the intermediate solution to form a more concentrated solution before crystallizing K_2SO_4 from the more concentrated solution.

4. The method of claim **1**, wherein crystallizing the recycle crystals from the first potassium-depleted liquor comprises sequentially evaporating a plurality of portions of water to recover potassium.

5. The method of claim **1**, wherein crystallizing langbeinite from the second potassium-depleted liquor comprises maintaining the second potassium-depleted liquor within a temperature range from about 70° C. to about 115° C.

6. The method of claim **5**, wherein crystallizing langbeinite from the second potassium-depleted liquor comprises maintaining the second potassium-depleted liquor within a temperature range from about 85° C. to about 100° C.

7. The method of claim **1**, wherein crystallizing langbeinite from the second potassium-depleted liquor comprises varying the production rate of langbeinite.

8. The method of claim **7**, wherein varying the production rate of langbeinite comprises alternately operating in at least two operating modes, wherein K_2SO_4 is formed in a first operating mode, and K_2SO_4 and langbeinite are each formed simultaneously in a second operating mode.

9. The method of claim **1**, further comprising recycling a portion of the second potassium-depleted liquor to mix with at least a portion of the first potassium-depleted liquor.

10. The method of claim **1**, further comprising mixing at least a portion of the second potassium-depleted liquor with K_2SO_4.

11. A method of processing a leach brine comprising potassium sulfate and magnesium sulfate, the method comprising:
    crystallizing K_2SO_4 from the leach brine to form a potassium-depleted liquor; and
    crystallizing langbeinite from the potassium-depleted liquor.

12. The method of claim **11**, further comprising decomposing at least a portion of the langbeinite to form at least one of leonite and schoenite.

13. The method of claim **12**, further comprising mixing at least a portion of the at least one of leonite and schoenite with the leach brine.

14. The method of claim **12**, further comprising decomposing at least a portion of the at least one of leonite and schoenite to form K_2SO_4.

15. A method of processing an aqueous solution comprising potassium sulfate and magnesium sulfate, the method comprising:

adding potassium, magnesium, and sulfate ions to the aqueous solution;

forming solid potassium sulfate and a concentrate; and

forming a second solid from at least a portion of the concentrate to form a potassium-depleted solution, the second solid comprising at least one material selected from the group consisting of langbeinite, leonite, schoenite, and potassium sulfate.

16. The method of claim **15**, wherein forming a second solid from at least a portion of the concentrate to form a potassium-depleted solution comprises forming langbeinite and decomposing at least a portion of the langbeinite to form at least one of leonite and schoenite.

17. The method of claim **15**, wherein adding potassium, magnesium, and sulfate ions to the aqueous solution comprises mixing at least a portion of the second solid with aqueous solution.

18. The method of claim **15**, wherein forming solid potassium sulfate and a concentrate comprises crystallizing and precipitating potassium sulfate.

19. The method of claim **15**, further comprising removing water from the aqueous solution.

20. The method of claim **15**, wherein forming a second solid from at least a portion of the concentrate to form a potassium-depleted solution comprises removing water from the concentration.

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