Danakil potash: $\text{K}_2\text{SO}_4$ across the Neogene: Implications, Part 4 of 4

How to deal with $\text{K}_2\text{SO}_4$

In this the fourth blog focusing on Danakil potash, we look at the potash geology of formerly mined Neogene deposits in Sicily and the Ukraine, then compare them and relevant processing techniques used to exploit their $\text{K}_2\text{SO}_4$ ore feeds. This information is then used to help guide a discussion of processing implications for potash extraction in the Danakil, where kainite is the dominant widespread potash salt. As seen in the previous three blogs there are other potash mineral styles present in the Danakil, which constitute more restricted ore fairways than the widespread bedded kainite, these other potash styles (deep meteoric - blog 2 of 4 and hydrothermal - blog 3 of 4), could be processed to extract MOP, but these other potash styles are also tied to high levels of $\text{MgCl}_2$, which must be dealt with in the brine processing stream. The most effective development combination is to understand the three occurrence styles, define appropriate specific brine processing streams and then combine the products in an single processing plant and then produce sulphate of potash (SOP), rather the Muriate of Potash (MOP), as SOP has a 30% price premium in current potash markets.

Kainite dominated the bedded potash ore feed in former mines in the Late Miocene (Messinian) sequence in Sicily and the Middle Miocene (Badenian) sequence in the Carpathian foredeep, Ukraine. Kainite also occurs in a number of potash deposits in the Permian of Germany and Russia. In Germany a combination of mined sylvinite and kieserite is used to manufacture sulphate of potash (SOP). Interestingly, Neogene and the Permian are times when world ocean waters were enriched in $\text{MgSO}_4$ (Lowenstein et al., 2001, 2003). In contrast, much of the Phanerozoic was typified by an ocean where $\text{MgSO}_4$ levels were less. It is from such marine brine feeds that most of the world’s larger Phanerozoic (SOP) potash ore deposits were precipitated (Warren, 2015). SOP is also produced from Quaternary Lake brines in China and Canada (see Cryogenic salt blog; 24 Feb. 2015).

SOP in Messinian evaporites, Sicily

A number of potash mines on the island extracted kainitite from the late Miocene Solofifera Series of Sicily (Figure 1). The last
of these mines closed in the mid-1990s, but portions of some are maintained and are still accessible for geotourism (eg Realmonte mine). The halite-hosted potash deposits are isolated ore bodies within two generally parallel troughs, 115 km long and 5-10 km wide, in the Caltanissetta Basin (Figure 1). They are separated by a thrust-related high 11-25 km wide and capped by the limestones of the “Calcari di Base". Kainite is the dominant potash mineral in the mined deposits. Across the basin, ore levels constitute six layers of variable thickness, with a grade of 10%-16% K₂O (pure kainite contains 18.9% K₂O), with very little insoluble content (0.4%-2.0%).

At the time the potash was deposited there was considerable tectonic activity in the area (Roveri et al. 2008, Manzi et al., 2011). Host sediments were deposited in piggy-back basins some 5.5 Ma atop a series of regional thrusts, so the ore layers have dips in the mines ranging up to 60° (Figure 2). Little if any of the limestone associated with the deposits was converted to dolomite, nor was the thick Messinian gypsum (upper and lower units), encasing the halite/kainite units, converted to anhydrite, it remains as gypsum with well preserved depositional textures.

However, the elevated salinities, and perhaps temperatures, required for kainite precipitation means anhydrite micronodes, observed in some ore levels, may be primary or syndepositional. A lack of carnallite, along with isotopic data, indicates that when the deposits were formed by the evaporation of the seawater, salinities did not usually proceed far past the kainite crystallization point (in contrast to Ethiopia where carnallite salinities typify the later stages of kainite deposition).

The largest Sicilian ore body was at Pasquasia, to the west of Caltanissetta, covering a 24 km² area at depths of 300-800 m (Figure 1). There were five ore beds at Pasquasia, all with highly undulating synclinal and anticlinal forms. The Number 2 bed was the thickest, averaging perhaps a 30-m thickness of 10.5% to 13.5% K₂O ore. The Pasquasia Mine was last operational from 1952 to 1992.

Ore geology remains somewhat more accessible at the former Realmonte mine, near the town of Agrigento. There, four main depositional units (A to D from base to top) typify the evaporite geology. As at Pasquasia, kainite was the targeted ore within a Messinian evaporite section that has total thickness of 400-600 m. As defined by Decima and Wezel, 1971, 1973; Decima, 1988, Lugli, 1999, the Realmonte mine section is made up of 4 units (Figure 2a):

- Unit A (up to 50 m thick): composed of evenly laminated grey halite with white anhydrite nodules and laminae that pass upward to grey massive halite beds.
- Unit B (total thickness ≈100 m): this potash entraining interval is dominated by mas-

Figure 2. Kainite in Sicily. A) Schematic showing potash stratigraphy in Realmonte Mine, Agrigento. B) Regional section of Messinian Geology in Realmonte region (after Decima and Wezel, 1971, 1973; Lugli, 1999).
Kainite is the main solid salt source in Neogene potash operations

Neogene seawater is MgSO₄ enriched compared to the bulk of Phanerozoic seawater time

- Unit C (70-80 m thick): is made up of white halite layers 10-20 cm thick, separated by irregular dark grey mud laminae and minor light grey polyhalite and anhydrite laminae (Figure 3).
- Unit D (60 m thick): is composed of a grey anhydritic mudstone (15-20 m thick), passing up into an anhydrite laminite sequence, followed by grey halite millimetre to centimetre layers intercalated with white anhydrite laminae.

According to Lugli, 1999, units A and B are made up of cumulates of well-sorted halite plate crystals, up to a few millimeters in size. Kainite typically forms discrete laminae and sutured crystal mosaic beds, ranging from a thickness of few mm to a maximum of 2 m, intercalated and embedded within unit B (Garcia-Veigas et al., 1995). It may also occur as small isometric crystals scattered within halite mosaics. Kainite textures are dominated by packed equant-granular mosaics, which show possible pressure-dissolution features at some grain boundaries. The associated halite layers are dominantly cumulates, which show no evidence of bottom overgrowth chevrons, implying evaporite precipitation was a "rain from heaven" pelagic style that took place in a stratified permanently subaqueous brine water body, possibly with a significant water depth to the bottom of the permanent lower water mass.

Only the uppermost part of potash bearing portion of unit B shows a progressive appearance of large halite rafts along with localized dissolution pits filled by mud, suggesting an upward shallowing of the basin at that time. In many parts of the Realmonte mine spectacular vertical fissures cut through the topmost part of unit B at the boundary with unit C, suggesting desiccation and subaerial exposure at this level (Lugli et al., 1999).

The overlying unit C is composed of cumulates of halite skeletal hoppers that evolve into halite chevrons illustrating bottom growth after foundering of the initial halite rafts. Halite layers in unit C show numerous dissolution pits filled by mud and irregular truncation of the upper crystal terminations, implying precipitation from a nonstratified, relatively shallow water body. Palaeo-temperatures of the brine that precipitated these halite crystals are highly variable from 22 to 32°C (Lugli and Lowenstein, 1997) and suggest a shallow hydrologically unstable body of water, unlike units A and B.

The bromine content of halite increases from the base of unit A to the horizons containing kainite (layer B) where it obtains values of up to 150 ppm. Upwards, the bromine content decreases once more to where at the top of Unit C it drops below 13 ppm, likely indicating a marked dilution of the mother brine. The dilution is likely a consequence of recycling (dissolution and reprecipitation) of previously deposited halite either by meteoric-continental waters (based on Br content; Decima 1978), or by seawater (based on the high sulphate concentration and significant potassium and magnesium content of fluid inclusions; Garcia-Veigas et al., 1995).

As in the Danakhil succession, evaporite precipitation at Realmonte began as halite-CaSO₄ interlayered succes-

Figure 3. Inclined halite-kainite bedding in the Realmonte Mine, Sicily. A illustrates the gentle dips at the tens-of-metres scale in this folded halite-kainite sequence, making it a suitable ore target. B.) Shows folded bedding at the tens-of-centimetres scale (lower left) related to mechanical strength contrasts. Image courtesy of Prinreset and Alberto Monte.
sion at the bottom of a stratified perennial water body, which shallowed and increased in concentration until reaching potash kainite saturation. In Sicily, this was followed by a period of exposure and desiccation indicated by the presence of giant megapoligonal structures. Finally, seawater flooded the salt pan again, dissolving and truncating part of the previous halite layers, which was then redeposited under shallow-water conditions at the bottom of a nonstratified (holomitic) water body (Lugli and Lowenstein, 1997, Lugli et al., 1999).

Unlike Ethiopia, the Neogene kainite deposits of Sicily were deposited in a thrust “piggy-back” basin setting and not in a rift sump (Figure 2b). Mineralogically similar, very thick, rift-related, now halokinetic, halite deposits of Middle Miocene age occur under the Red Sea’s coastal plain between Jizan, Saudi Arabia (where they outcrop) to Safaga, Egypt, with limited potash is found in some Red Sea locations at depths suitable for solution mining (Notholt 1983; Garrett, 1995). Potash-enriched marine end-liquor brines characterise Red Sea geothermal springs, implying a more sizeable potash mass may be (or once have been) present in this region. Hite and Wassef (1983) argue gamma ray peaks in two drill hole logs in this area suggest the presence of sylvite, carnallite and possibly langbeinite at depth.

**K₂SO₄ salts in Miocene of Ukraine**

Miocene salt deposits occur in the western Ukraine within two structural terranes: 1) Carpathian Foredeep (rock and potash salt) and (II) Transcarpathian trough (rock salt) (Figure 4a). These salt-bearing deposits differ in the thickness and lithology depending on the regional tectonic location (Czapowski et al., 2009). In the Ukrainian part of Carpathian Foredeep, three main tectonic zones were distinguished (Figure 4b): (I) outer zone (Bilche-Volytsya Unit), in which the Miocene molasse deposits overlie discordantly the Mesozoic platform basement at the depth of 10-200 m, and in the foredeep they subsided under the overthrust.

![Figure 4. Potash in Carpathian Foredeep, Ukraine. A) Distribution of potash and rock salt deposits (red areas, salt mines marked by green circles, olerd saltworks by grey circles) plotted on a background of the regional geological structure of western Ukraine (after ).B) Geological cross-section of Carpathian Foredeep near Stebnyk (after Bukowski and Czapowski, 2009; Hryniv et al., 2007; Koriń, 1994). See Figure 5 for stratigraphic detail.](https://www.saltworkconsultants.com)
of the Sambir zone and are at depths of 1.2–2.2 km (Bukowski and Czapowski, 2009; Hryniv et al., 2007); (II) central zone (Sambir Unit), in which the Miocene deposits were overthrust some 8–12 km onto the external part of the Foredeep deposits of the external zone occur at depths of 1.0–2.2 km; (III) internal zone (Boryslav–Pokuttya Unit), where Miocene deposits were overthrust atop the Sambir Nappe zone across a distance of some 25 km (Hryniv et al., 2007).

The Carpathian Foredeep formed during the Early Miocene, located north of emerging the Outer (Flysch) Carpathians. This basin was filled with Miocene siliciclastic deposits (clays, claystones, sandstones and conglomerates) with a maximum thickness of 3 km in Poland and up to 5 km in Ukraine (Oszczypko, 2006). Two main evaporite bearing formations characterise the saline portions of the succession and were precipitated when the hydrographic connection to the Miocene ocean was severely reduced or lost (Figures 4, 5): A) Vorotyshcha Beds, dated as Late Egenburgian and Ottnangian, some 1.1–2.3 km thick and composed of clays with sandstones, with exploitable rocksalt and potash salt interbeds. This suite is further subdivided into two subsuites: a) a lower unit, some 100–900 m thick with rock salt beds and, b) an upper unit, some 0.7–1.0 km thick, with significant potash beds, now deformed (Hryniv et al., 2007). The Stebnyk potash mine is located in this lower subset in the Boryslav–Pokuttya zone, close to the Carpathian overthrust); B) Tyras Beds of Badenian age reach thicknesses of 300–800 m in the Sambir and Bilche-Volytsya units and are dominated by salt breccias and contain both rock and potash salts. Thicknesses in the Bilche-Volytsya Unit range from 20–70 m and are made up of a combination of claystones, sandstones, carbonates, sulphates and rock salts with little or no potash.

Hence, potash salts of the Carpathian Foredeep are related either to the Vorotyshcha Beds located in the Boryslav–Pokuttya zone, or to the Tyras Beds (Badenian) in the Sambir zone (Figure 5). These associations range across different ages, but have many similar features, such as large number of potash lenses in the section, mostly in folded-thrust setting, and owing to their likely Neogene–marine mother brine contain many sulphate salts, along with a high clay content. Accordingly, the main potash ore salts are kainite, langbeinite and kainite–langbeinite mixtures. Hryniv et al. (2007) note more than 20 salt minerals in the Miocene potash levels and in their weathering products. Bromine contents in halites of the Carpathian Foredeep for deposits without potash salts range from 10 to 100 ppm (on average 56 ppm); in halite from salt breccias with potash salts range from 30 to 230 ppm (average 120 ppm); and in halite from potash beds ranges from 70 to 300 ppm (average 170 ppm). In the ore minerals from the main potash deposits, bromine content ranges are: a) in kainite 800–2300 ppm; b) in sylvite 1410–
2660 ppm; and c) in carnallite 1520–2450 ppm. This is consistent with kainite being a somewhat less saline precipitate than carnallite/sylvite (Figure 6).

The brines of Vorotyshcha and Tyras salt-forming basins (based on data from brine inclusions in an investigation of sedimentary halite, listed by Hryniv et al. (2007), are consistent with mother brines of the Na–K–Mg–Cl–SO₄ (MgSO₄-rich) chemical type (consistent with a Neogene marine source). Inclusion analysis indicates the temperature of halite formation in the Miocene basin brines in Forecarpathian region was around 25°C. During the potash (Kainite) stages it is likely these solutions became perennially stratified and heliothermal so that the bottom brines could be heated to 40–60°C, more than double the temperature of the brine surface layer (see Warren, 2015 for a discussion of the relevant physical chemistry and brine stratification styles). During later burial and catagenesis the temperatures preserved in recrystallised halites are as high as 70°C with a clear regional tectonic distribution (Hryniv et al. (2007).

Maximum potash salt production was achieved under Soviet supervision in the 1960s, when the Stebnyk and Kalush mines delivered 150 x 10⁶ tonnes of K₂O and the “New” Stebnyk salt-works some 250 x 10⁶ tonnes as K₂SO₄ per year.

Stebnyk potash (Figure 7a)

The potash salt deposit in the Stebnyk ore field occurs within the Miocene (Eggenburgian) Vorotyshcha Beds (Figures 4, 5). Salt-bearing deposits in the Stebnyk area were traditionally attributed to two main rock complexes (Lower and Upper Vorotyshcha Beds) separated by terrigenous (sandstones and conglomerates) Zahirsk Beds (Petryczenko et al., 1994). More recent work indicates that the Zahirsk Beds belonged to aolistostrome horizon (a submarine slump, interrupting evaporite deposition) and there are no valid arguments for subdividing the Vorotyshcha Beds into two subunits (Hryniv et al., 2007).

There are multiple salt-bearing series in the Stebnyk deposit (Figure 4b) and their total thickness ranges up to 2,000 m in responses to intensive fold thickening and overthrusting of the Carpathians foredeep. Intervals with more fluid salt mineralogies were compressed and squeezed into the centers of synclinal folds, to form a number of elongate lens-shape ore bodies (Figure 4b). These bodies are often several hundreds meters wide and in mineable zones occur at the depth of 80-650 m, typically at 100-360 m.

The lower part of the Vorotyshcha Suite (Beds) in the Stebnyk Mine area is composed of a salt-bearing breccia, with sylvinitic or carnallitite interlayers typically in its upper parts, as well as numerous blocks of folded marly clays (Bukowski and Czapowski, 2009). Above this is the potash-bearing ore series, some 10-125 m thick and, composed of beds of kainite, langbeinite and lagbeinite-kainite with local sylvinitic and kieserite (Hryniv et al., 2007). The potash interval is overlain by a rock salt complex some 60 m thick (Koriń, 1994).

The Stebnyk plant is now abandoned and in disrepair. In 1983 there was a major environmental disaster (explosion) at a nearby chemical plant (in the ammonia manufacture section), which was supplied chemical feedstock by the mine. No lives were lost, but damage at the plant, tied to the explosion, released some 4.6 million cubic metric of thick brine from an earthen storage dam into the nearby Dniester River. At the time this river was probably the least environmentally damaged by industrial operations under Soviet administration. The spill disrupted water supplies to millions of people along the river, killed hundreds of tons of fish, destroyed river vegetation and deposited a million tons of mineral salts on the bottom of a 30-mile-long reservoir on the Dniester. Stebnik is located in the Ukrainian province of Lvov. Staff members at the United States Embassy at the time seized on the name to dub the incident “Lvov Canal,” after the Love Canal contamination in the United States.
Kalush potash salt geology (Figure 7b)

Thickness of Miocene (Badenian) deposits near the Kalush Mine is around 1 km (Figures 4a). Two local salt units (beds) are distinguished within the Tyras Beds: the Kalush and Holyn suites, which constitute the nucleus of Miocene deposits of Sambir Unit (Figure 5). Beds have been overthrust and folded onto the Mesozoic and Middle to Upper Miocene molasse sediments of the outer (Bilche-Volysya) tectonic unit (Figure 4b). The Kalush Beds are 50-170 m thick, mostly clays, with sandstone and mudstone intercalations. In contrast the Holyn beds are more saline and dominated by clayey rock salts (30-60% of clay), salty clays and claystones (Koriń, 1994). Repeated interbeds and concentrations of potash salts up to several meters thick within the Holyn beds define a number of separate potash salt fields in the Kalush area (Figures 4b, 5). Such salt seams are dominated by several MgSO₄-enriched mineralogies: kainite, langbeinite-kainite, langbeinite, sylvinites and less much uncommon carnallite and polyhalite. These polymetallogenic sulphate ore mineral assemblages are co-associated with anhydrite, kieserite and various carbonates. The potash ore fields typically occur in tectonic troughs within larger synclines, usually at depths of 100-150 m, to a maximum of 800 m.

Conventional processing streams for manufacture of SOP and MOP

To date the main natural sulphate salts that have been successfully processed to manufacture sulphate of potash (SOP) are:

- Kainite (KCl·MgSO₄·3H₂O) (as in Sicily - potash mines are no longer active)
- Kieserite (MgSO₄·H₂O) (as in Zechstein, Germany - some potash mines active)
- Langbeinite (K₂SO₄·2MgSO₄) (as in Carlsbad, New Mexico - active potash mine)
- Polyminalic sulphate ores (as in the Stebnyk and Kalush ores, Ukraine - these potash mines are no longer active)

All the processing approaches deal with a mixed sulphate salt or complex sulphate brine feed and involve conversion to form an intermediate doublesalt product, usually schoenite (or leonite at elevated temperatures) or glaserite. This intermediate is then water-leached to obtain SOP.

For example, with a kainite feed, the process involves the following reactions:

$$2\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{MgCl}_2$$

followed by water-leaching of the schoenite intermediate

$$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{MgSO}_4 + 6\text{H}_2\text{O}$$

In Sicily in the 1960s and 70s, the Italian miners utilized such a solid kainitite ore feed, from conventional underground mining and leaching approaches. The various Italian mines were heavily government subsidized and in terms of a free-standing operation most were never truly profitable. The main kainitite processing technique used in Sicily, is similar in many ways to that used to create SOP from winter-precipitated cryogenic salt slurries in pans that were purpose-constructed in the North Arm area of in Great Salt Lake, Utah (Table 1; see Warren, 2015 for details on Great Salt Lake operations). The Italian extraction method required crushing and flotation to create a fine-sized kainite ore feed with less than 5% NaCl. This product was then leached at temperatures greater than 90°C with an epsomite brine and converted into a langbeinite slurry, a portion which was then reacted with a schoenite brine to precipitate potassium chloride and epsomite solids, which were then separated from each other and from the epsomite brine. A portion of the potassium chloride was then reacted with magnesium sulphate in the presence of a sulphate brine to create schoenite and a schoenite brine. This schoenite brine was recycled and the remaining potassium chloride reacted with the schoenite in the presence of water, to obtain potassium sulphate and a sulphate brine.

The processing stream in the Ukraine was similar for the various Carpathian ore feeds, which “out-of-mine-face” typically contained around 9% potassium and 15% clay and so were a less pure input to the processing stream, compared to the typical mine face product in Sicily. Like Sicily, schoenite was the main intermediate salt. Ore was leached with a hot synthetic kainite solution in a dissolution chamber. The langbeinite, polyhalite and halite remained undissolved in the chamber. Salts and clay were then moved into a Dorr-Oliver settler where the clays were allowed to settle and were then moved to a washer and discarded. The remaining solution was crystallized at the proper cation and anion proportions to produce crystalline schoenite. To avoid precipitation of potassium chloride and sodium chloride, a saturated solution of potassium and magnesium sulfate was added to the Dorr-Oliver settler. The resulting slurry of schoenite was filtered and crystals were leached with water to produce K₂SO₄ crystals, which were centrifuged and recycled and a liquor of potassium and magnesium sulfates obtained. The liquid phase from the filter was recycled and added to the schoenite liquor from obtaonned by vacuum crystallization. Part of the schoenite liquor was evaporated to produce crystalline sodium sulfate, while the magnesium chloride liquid end product was discarded. The slurry from the evaporation unit was recycled as “synthetic kainite.” This process stream permitted the use of the relatively low quality Carpathian ore and produced several commercially valuable products including potassium sulfate, potassium-magnesium sulfate, potassium chloride, sodium sulfate and magnesium.
Table 1. Conventional methods of Sulphate of Potash manufacture

<table>
<thead>
<tr>
<th>Method for making K₂SO₄</th>
<th>Raw materials</th>
<th>Detail of Sulphate of Potash (SOP) production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion of sulphuric acid (H₂SO₄)</td>
<td>Byproduct of HCl acid</td>
<td>Potassium sulfate can be synthesized by reaction of potassium chloride with sulfuric acid according to the Mannheim industrial process. Potassium sulfate is produced according to the following reaction: 2 KCl + H₂SO₄ → 2HCl + K₂SO₄. This method for producing SOP accounts for 50% to 60% of the global production of sulphate of potash. The Mannheim Process is the most expensive method of producing SOP due to energy requirements and high cost of purchasing MOP and sulphuric acid.</td>
</tr>
<tr>
<td>Decomposition of schoenite (K₂SO₄·MgSO₄·6H₂O)</td>
<td>Lake brines, Kainite ore</td>
<td>Some operations produce SOP from the salt mixtures harvested from natural brines. Three companies can produce potassium sulfate from natural brines in such a way on a large scale: GSL Minerals (Great Salt Lake, Utah), SQM (Salar de Atacama, northern Chile) and Luobupo Potash (Lop Nur, northwest China). This method requires brines with high sulfate levels such as those found naturally within these salt lakes. The sulfate is typically present in the form of the double salt kainite, which is converted to schoenite by leaching with a sulfate brine. The leach process is hampered by high sodium chloride content in the harvest salts and the halite is first removed by flotation. After thickening, the schoenite is decomposed by simply adding hot water, whereupon the magnesium sulfate enters solution leaving SOP crystals. This process is currently the lowest cost method to make SOP.</td>
</tr>
<tr>
<td>Conversion of kieserite (MgSO₄·H₂O)</td>
<td>Underground ore + KCl</td>
<td>Historically this was the main method of SOP manufacture utilising mine kieserite and sylvite ores extracted by conventional mining techniques in the Permian Zechstein salt series of Germany. Once again this process involves the creation of a kainite to schoenite intermediate and its subsequent processing into SOP as outlined above: MgSO₄·H₂O + KCl → KCl·MgSO₄·3H₂O.</td>
</tr>
<tr>
<td>Decomposition of langbeinite (K₂SO₄·2MgSO₄)</td>
<td>Underground langbeinite ore, or mixtures of kainite and sylvite</td>
<td>The production of potassium sulfate from langbeinite is possible when significant muriate of potash is available either separately or as sylvite in the same ore stream. The langbeinite ore is separated from sylvite and halite by selective washing, froth flotation, or heavy media separation. Langbeinite used in the process must be pulverized in ball mills, and the resulting fine powder is mixed with a solution of the muriate of potash. The muriate of potash is dissolved and clarified in a separate unit. The reaction, in the presence of water, yields potassium sulfate in a crystalline form and a brine. Crystals are centrifuged or filtered, dried in a rotary dryer, sized and finished. The finished methods either produce coarse material or granulated product. Any residual mixed salts are added to a sulfate reactor and the liquor is discarded as a waste.</td>
</tr>
<tr>
<td>Decomposition of glaserite (K₂SO₄·Na₂SO₄·KCl; Na₂SO₄·KCl)</td>
<td>KCl • Salt cake, Glauber salt, Burkeite, KCl • Glauber salt, Quaternary lakes (Sealees Lake)</td>
<td>Potassium chloride can be reacted with various sulfate salts to form a glaserite double salt that can be decomposed to yield potassium sulfate. The most common raw material employed for this purpose is sodium sulfate. Sodium sulfate, either in the form of mirabilite (also known as Glauber's Salt) or sulfate brine, is treated with brine saturated with MOP to produce glaserite. The glaserite is separated and treated with fresh MOP brine, decomposing into potassium sulfate and sodium chloride. These methods of production are the second greatest source of global supply at 25% to 30%.</td>
</tr>
</tbody>
</table>

Can Danakhil potash be economically mined?

For any potash deposit (MOP or SOP) there are three approaches that are used today to economically extract ore (Warren 2015): 1) Conventional underground mining, 2) Processing of lake brines 3) Solution mining and surface processing of brines. Historically, method 1 and 2 have been successfully conducted in the Danakhil Depression, although method 1) was terminated in the Dallol area by a mine flood.

Conventional mining

To achieve a successful conventional underground MOP potash mine any where in the world, ideally requires (Warren, 2015): 1) A low dipping, laterally continuous and consistently predictable quality ore target, not subject to substantial changes in bed dip or continuity. 2) An ore grade of 14% K₂O or higher, and bed thickness of more than 1.2 m. 3) Around 8-m of impervious salt in the mine back or roof, although some potash mines, such as the Bouby mine in the UK are working with < 2 meters of salt in the back (but there the extraction is automated and the access roads approach the target ore zone from below). 4) An initial access shaft that is vertical and typically dug using ground freezing techniques to prevent unwanted water entry during excavation. 5) A typical ore depth in the range 500-1100 metres. Shallower mines are subject to unpredictable water entry/flooding and catastrophic roof collapse, as in the Cis-Urals region (see Solikamsk blog; Feb 19, 2015). Mines deeper than 1000-1100 metres are at the limit of conventional
mining and the salt surround is subject to substantial creep and possible explosive pressure release outbursts (as in some potash mines in the former East Germany). 6) At-surface and in-mine conditions not subject to damage by earthquakes, water floods or volcanism.

During the feasibility phase of the Parsons Mining Project it became evident that the halite material overlying the Sylvinite Member was porous and that there was no adequate hydrologic protection layer above the Sylvinite Member. In my mind, this is further evidence of the hydrologic access needed to convert carnallite to sylvite along the bajada chemical front (see previous blog). In any event the absence of a hydrologic protection layer above the Sylvinite Member means that conventional underground mining is not feasible for this type of potash. In addition, given the tectonic instability of the Danakhil Depression it is likely that no underground conventional mine is feasible in the hydrologically, seismically and hydrothermally active setting, which is the Danakhil depression, even if planning to exploit the deeper widespread kainitite beds (>350-450m)

Some explorers in the Danakhil depression, especially on the Eritrean side are proposing to use surface or open-pit mining (quarrying) approaches to reach and extract/processing shallow ore salts. For this approach to be successful requires the shallow potash targets to be above regional groundwater level. Depths to the different ore targets on the Ethiopian side of the depression range between 45m and 600m and almost all lie below the regional water. Also, to access the mineralised material a large volume of variably water-saturated overburden would need to be removed. Even if areas with ore levels above the water table do exist on the Ethiopian side, the whole of the Danakhil sump is subject to periodic runoff and sheetfloods, sourced in the western highlands. Open pit areas would be regularly flooded during the lifetime of the pit, resulting in a need for extensive dewatering. For these reasons, and the possibility of earthquake damage, open pit mining is likely not feasible.

Can the Danakhil potash be solution mined?

To achieve this, brines extracted from different mineralogical levels and ore types will need to be individually targeted and kept as separate feeds into dedicated at-surface processing streams. On the Dallol surface, there are numerous sites that are suitable for pan construction, the climate is suitable for natural solar concentration as the region is typically dry, flat and hyperarid. If the potash zones in the Dallol depression are to be economically exploited via solution mining it will likely first require an understanding of the geometries of the 3 different forms of potash, namely; 1) Bedded kainitite-carnallitite (widespread in the depression), 2) Diagenetic sylvite via incongruent dissolution (focused by deep meteoric mixing and the bajada chemical interface along the western margin. 3) Hydrothermal potash (largely found in the vicinity of Dallol mound). Next, in order to have known-chemistry feedstocks into a SOP chemical plant, it will require the appropriate application of extraction/solution mining chemistries for each of these deposit styles. This would involve the construction of dedicated brine fields and the pumping of shallow Dallol brines (mostly from <200-250m below the surface) into a series of minerallogically-separated at-surface solar concentrator pans.

There are some subsurface aspects that need to be considered and controlled in a solution mining approach in the Danakhil. The first is the possibility of uncontrolled solution cavity stoping (for example, where a solution cavity blanket layer is lost due to cavity intersection with an unexpected zone of high permeability). If cavity shape is not closely monitored (for example by regular downhole sonar scans) and controlled, this could ultimately lead to the collapse of the land surface atop regions of shallow evaporites (<150-200 below the surface). As we saw in blog 3, doline collapse is a natural process in the Dallol Mound region, as it is any region of shallow soluble evaporites in contact with undersaturated pore waters. Ongoing natural solution via interaction with hydrothermal waters has created the colorful brine springs that attract tourists to the Dallol Mound region. But a operator does not want new dolines to daylight in their brine field, as environmental advocates would quickly lay blame at the feet of the brinefield operator. For this reason, the region in the vicinity of the Dallol Mount (eg the “Crescent deposit”) should probably be avoided.

Most modern brinefield operators prefer a slowly-dissolving targeted salt bed that is at least 400-500m below the land surface (Warren, 2015). This broadens and lessens the intensity of the cone of ground collapse above the extraction zone and so lessens the possibility of catastrophic surface collapse. Use of a diesel rather than air blanket during cavity operation is also preferred because of potential porosity intersections at the base of the Upper Rock Salt (URF) contact (see blog 2 in the Danakhil blogs) Appropriate deeper potash beds in the Danakhil are laterally continuous beds of kainitite with lesser carnallitite. Drilling to date has identified little sylvite or bischofite in these widespread layers. This simplifies the mineral input chemistry in terms of a kainite target located further out in the saltflat, with a sylvite or sylvite bischofite operation closer toward the western margin. However, there are no currently active solution mines solely targeting a kainite ore anywhere in the world and a processing scheme would need to be developed.
This leads to another consideration with a solution mining approach in the Danakhil depression, and that is that there are no existing brine technologies that can deal economically with high concurrent levels of magnesium and possibly-elevated sulphate levels in a recovered brine feed. The third consideration is reliably predicting the occurrence of, and avoiding, any metre- to decametre-scale brine-filled cavities that the drilling has shown are not uncommon at the sylvinite-bischofite-carnallite level in the Dallol stratigraphy along the Bajada chemistry zone. Intersecting and slowly dewatering such large brine cavities may not lead to at-surface ground collapse, but if not identified could create unexpected variations in the ionic proportions of brine feeds into the solar concentrators (for example drilling has identified subsurface regions dominated by bischofite, which is one of the most soluble bittern salts in the Danakhil depression - see Ercospan 2010, 2011 for drill result summaries).

**Solution mining is a more cost effective and safer approach to potash extraction in the Danakhil Depression**

**And So?**

So, at this stage, there are encouraging possibilities for economic recovery of both MOP and SOP from solution brines pumped to chemistry-specific solar pans in the Danakhil. Processing chemistry will require further site-specific studies to see which of the current known methods or their modification is economically feasible for SOP and perhaps combined SOP and MOP manufacture in the hyperarid climate of the Danakhil, as is being currently done by Allana Potash. It is also possible that a new processing stream chemistry could be developed for the Dallol brines, in order to deal with very high concurrent levels of MgCl2 (widespread bischofite beds), or develop new or modify existing processing streams that target kainitite at depth. Similar K2SO4 brine processing chemistries have been applied in pans of the margins of the Great Salt Lake. But there salt pan processing was in part seasonally cryogenic, something that the Dallol climate certainly is not, so it is likely modified or new approaches to year-round pan management will be required.

Any future potash operation in the Danakhil will have to compete in product pricing with well established, high-volume low cost producers in Canada, Belarus and Russia (Figure 8). Today, establishing a new conventional underground MOP potash mine is associated with setup costs well in excess of a billion dollars (US$). The costs are high as the entry shaft to a conventional underground mine must be completed without water entry and is usually done via ground freezing. This is the approach currently underway at BHP’s MOP Jansen Mine in Saskatchewan, Canada. Because of the very high costs involved in underground entry construction, and the well established nature of the competition, the proved amount of ore for a conventional mine should be sufficient for at least 20 years of production (subject to a given mill size, mill recovery rate for a given ore depth and the density and origin of salt “horses”). Kogel et al. (2006) states any potash plant or mill should be at capable of least 300,000 t K2O per annum in order to compete with a number of established plants with nameplate capacity in excess of 1 Mt.

In contrast, the shallow nature of a Danakhil potash source means cheaper access costs, while a solution well approach makes for much cheaper and shorter approach times for brine/ore extraction, providing suitable economic brine processing streams are available (Figure 8). Potash is a mine product where transport to market is a very considerable cost proportion in terms of an operation’s profitability. The location of the Danakhil gives it a low-cost transport advantage as a future supplier to the ever-growing agricultural markets of Africa, India and perhaps China. And finally, a potassium sulphate product has a 30% cost premium over a muriate of potash (KCl) product.
References


