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Historical and technical developments of potassium resources

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The mining of soluble potassium salts (potash) is essential for manufacturing fertilizers required to ensure continuous production of crops and hence global food security. As of 2014, potash is mined predominantly in the northern hemisphere, where large deposits occur. Production tonnage and prices do not take into account the needs of the farmers of the poorest countries. Consequently, soils of some regions of the southern hemisphere are currently being depleted of potassium due to the expansion and intensification of agriculture coupled with the lack of affordable potash. Moving away from mined salts towards locally available resources of potassium, such as K-bearing silicates, could be one option to improve this situation. Overall, the global potash production system and its sustainability warrant discussion. In this contribution we examine the history of potash production, and discuss the different sources and technologies used throughout the centuries. In particular, we highlight the political and economic conditions that favored the development of one specific technology over another. We identified a pattern of needs driving innovation. We show that as needs evolved throughout history, alternatives to soluble salts have been used to obtain K-fertilizers. Those alternatives may meet the incoming needs of our century, providing the regulatory and advisory practices that prevailed in the 20th century are revised.

Keywords: Potash, industrial history, fertilizers, sustainability, food security

Highlights:
- The development of the potash industry from 1700 to the present days is reviewed
- A historical analysis reveals the origin of the current limitations of the potash market
- Past experiences provide guidelines for the successful development of a new generation of potash fertilizers
1. INTRODUCTION

Fertilizers are an essential component of crop production (Scherer et al., 2002) particularly to replace nutrients removed from the soil during harvesting (referred to as ‘oftake’; Sheldrick et al., 2002). The main elements provided by fertilizers are nitrogen (N), phosphorus (P) and potassium (K) (Lüttge and Clarkson, 1989, Scherer et al., 2002). N and P are essential building blocks of nucleic acids and adenosine triphosphate (ATP), the biological energy carrier (Frink et al., 1999; Smil, 2004). K is necessary to regulate the electrochemical (and osmotic) potential across the cell membrane (Darst, 1991; Lüttge and Clarkson, 1989; Öborn et al., 2005; Römheld and Kirkby, 2010). N-fertilizers are manufactured from ammonia which is synthesized with the Haber-Bosch process using N₂ from the air and H₂ from fossil fuels as reactants (Hager, 2008; Smil, 2004; Russel and Williams, 1977). P- and K-fertilizers are products of the mining industry (Manning, 2010; Russel and Williams, 1977). P-fertilizers are obtained from phosphate rocks containing the mineral apatite (MacDonald et al., 2011; Manning, 2010; Manning, 2012; Obersteiner et al., 2013; Scholtz and Wellmer, 2013). K-fertilizers are presently obtained from sedimentary rocks (Supplementary Material) that are mixtures of soluble salts (most importantly KCl) referred to as potash when traded as a commodity. Although the K⁺ ion is the form of potassium released by commercial fertilizers, the total K content in different potash products is conventionally expressed as equivalent weight percent of potassium oxide (wt % K₂O).

Our anthropocene era (Crutzen, 2002) sees a complex interplay of human activities that outcompetes Nature in both time and space, thus resulting in a force of geological relevance (Crutzen, 2002; Crutzen, 2006). Since the industrial revolution, mining significantly contributes to anthropogenic geological change (Azapagic, 2004; Crutzen, 2002). The pressing challenge for human development is to formulate a model for progress which meets the needs of the present without compromising the ability of future generations to meet their own needs (Brundtland, 1987). The underlying concept is sustainability, a multidimensional construct that according to a classic approach comprises three main domains: i) society ii) economy and iii) environment (Azapagic, 2004; Brown et al., 1987; Cordell et al., 2009; Costanza and Patten, 1995; Dold, 2008; Lélé, 1991; Leonards et al. 2000; Tilman et al., 2002). In this framework the shortcomings of current industrial paradigms, fertilizers included, are noteworthy.

Societies currently need fertilizers to improve agricultural yields and ensure food security. Concerns have been raised on the scarcity of non-renewable P reserves (Cordell et al., 2009). Although such concerns have been proved to be unjustified (Scholtz and Wellmer, 2013) and part of a historically recurring debate (Ulrich and Frossard, 2014), the problem of the accessibility of fertilizers from the poorest societies remains less discussed. Phosphate rocks are mined in more than thirty countries dominated by China, USA and Morocco (Cordell et al., 2009; Manning, 2012; Obersteiner et al., 2013). In the case of potash, scarcity of reserves has not been reported so far. Ores are expected to last about 400 years at the current rate of extraction, based on estimates published by the United States Geological Survey (Jasinski, 2011). However, potash production is strongly dominated by three countries: Canada, Russia and Belarus produce more than 90% of world potash (Anderson, 1985; The New York Times Editorial Board, 2013; Manning, 2010; Manning, 2012, Rittenhouse 1979). Thus, in the Global South large amounts of potash have to be imported from the northern hemisphere. An emblematic example is given by Brazil that in 2011 imported 4,357,186 t of K₂O, more than 90% of its current potash need (FAOSTAT database, 2013). Approaches towards national self-sufficiency may be sought for, especially for developing countries, to allow stronger negotiation position on both the international stage and the agricultural world markets.

Economy is the primary driver of industries, fertilizers included. Overall, global potash revenues accounted for US$26 billion in 2012 (Manning, 2012). A common impression is that the limited geographical distribution of
productive potash mines can result in trades that favor producers rather than buyers (The New York Times Editorial Board, 2013). As an example, the potash market experienced a certain degree of monopolization and price cartelization at its inception, thus shaping its current status (Anderson, 1985; Hayes, 1942; Kreps, 1931; Kurrelmeyer, 1951; Tosdal, 1913). The free-on-board price for one tonne of potash peaked at US$800 in 2008. Since then, price has been falling due to major market readjustments, but remains high for many farmers (about US$300/t F.O.B as of 2014), in part reflecting the initial capital cost of the few deep mines in exploitation. Most importantly, inefficient logistics and infrastructure increase the final cost for the farmers in the poorest countries. In particular, fertilizer use statistics for Africa demonstrate that despite supporting 15% of the world’s population, this continent only uses 1.5% of the world’s K fertilizers (Manning 2012), an unsustainable situation in the perspective of its continuous population growth. Exploration for and opening of conventional deep mines are lengthy and costly processes that seem impractical for the Global South. Thus, new paradigms for the current potash market could be proposed to meet the needs of those who cannot access fertilizers on the grounds of cost or availability.

Environment is the third imperative that a sustainable model needs to confront. Current mining activities raise questions on deterioration of air and water quality as well as landscape modification/degradation (Azapagic, 2004; Dold, 2008; Anonymous, 2001; Russel and Williams, 1977). From a soil perspective the imbalance in offtake through cropping impoverishes the quality of the soil. However, different situations are observed for the three main nutrients. N is approximately in balance in the world soils meaning that agronomic inputs (fertilizers plus manure) equal the outputs (crop harvests; Sheldrick et al., 2002). Similarly, P global inputs exceeded the outputs in the year 2000, although 30% of the global cropland still experienced a deficit (MacDonald et al., 2011). Balanced levels of N and P in soils that are subject to through drainage suggest excessive application of fertilizers that leads to the critical problem of eutrophication of the aquatic ecosystems (Cordell et al., 2009; Frink et al., 1999). For K, in contrast, deficits have been reported especially for the African continent (Sheldrick and Lingard, 2004) as well as for China and India (Römhild and Kirkby, 2010). Significant reduction in K use has been observed also in many European countries (Öborn et al., 2005; Somerwill et al., 2012). Low K levels suggest agronomic practices overly intense with respect to the amount of potash replenished by fertilizers. If potassium deficits are not corrected, fertility loss will have to be faced. While such correction can be relatively easily implemented in the northern hemisphere, the deep leached soils of the Global South might be at risk. Furthermore, even if actual potash fertilizers from the North should reach the South, a high carbon cost for transportation, along with the effects of salinization and chloride, or loss through drainage, will have to be handled (Bernstein, 1975; Cordell et al., 2009; Lodge, 1938; Rozema and Flowers, 2008). Alternative approaches have been put forward. For example, the concept of agrogeology proposed as early as 1862 and redefined by van Straaten, aims at fertilizing the soils of the Global South by using slow nutrient releasers of geological origin such as unprocessed P- or K- bearing rocks (petrofertilizers) (De’sigmond, 1935; Leonardos et al., 1987; Leonardos et al., 2000; Van Straaten, 2002; Van Straaten, 2006). Movements such as Rochagem have promoted this concept (remineralize.org, 2014).

Overall, concerns on the possibility of a sustainable agriculture for the 21st century seem justified and the role of fertilizers appears pivotal. In this paper we focus on K-fertilizers. The sustainability challenge is to develop a potash market that takes into account affordability, local availability and compatibility with crops and soil composition (Van Straaten, 2006). To achieve this market, it is essential to understand the historical and social context (Cordell et al., 2009; Scholtz and Wellmer, 2013; Ulrich and Frossard, 2014) that has led to the present-day situation. Therefore, this paper addresses the history of potash production from 1700 to the present on the basis of several multidisciplinary sources. The intimate interconnections between geopolitical, economic and technological factors that have led to the current potash sector are highlighted. Food security and the possibility
of reducing the gap between need and access to potash may very well depend on a holistic interpretation of such interconnections.

2. POTASH PRODUCTION THROUGH THE INDUSTRIAL REVOLUTION: 1700-1910

K, from the neo-Latin *kalium* (derived from ‘alkali’, Latinized form of the Arabic *al-kali* meaning calcined ash), was isolated as an element by Humphry Davy in 1807 but its compounds were used in processes known since ancient times (Supplementary Material). At a global scale, the leaching of wood ashes was the dominant route for the synthesis of potash compounds until about 1860, inheriting methods developed prior to the birth of industrial chemistry (Figure 1) (Kreps, 1931; Miller, 1980; Östlund et al., 1998). In Europe, the wood ash market was largely dominated by Russia, which could rely on constant supplies from extensive forests (Browne, 1926; Miller, 1980; Östlund et al., 1998). During the 17th century two additional sources of ashes were halophyte plants from Mediterranean countries (barilla) and algae harvested in northern Europe (kelp) (Ashtor and Cevidalli, 1983; Browne, 1926; Clow and Clow, 1947; Kreps, 1931; Miller, 1980; Neushul, 1989; Tite et al., 2006). In 1650 trades between England and Russia were interrupted due to political disputes causing a general spike in the price of barilla (Kreps, 1931). It was the first act of a series of tension and warfare events that pervaded Europe throughout the 18th century and that made problematic the supply of barilla. Furthermore, scarcity of lumber had become widespread, contributing to an increase in the price of wood ashes (Browne, 1926; Clow and Clow, 1947; Kreps, 1931; Östlund et al., 1998). It is in this period that potash emerges as a strategic commodity at the center of national interests. Under the joint effect of periodic shortages, high demand and prices as well as market monopolization by Russia and Sweden, the development of a local potash sector became a priority in England. In the next sections we discuss the establishment of the kelp industry in Scotland and the wood ash industry in the American colonies. As detailed in Section 2.3, this latter industry disappeared by the middle of the 19th century, mainly because of the opening of potash mines in Stassfurt, Germany (Figure 1).

2.1. The Scottish kelp industry

Significant kelp (ash) trade developed during the 17th and 18th century, especially in northern Europe (France, Ireland, Norway and Scotland), where large quantities of seaweeds were strewn on the coasts (Clow and Clow, 1947; Neushul, 1989; Thieme, 2002). This biomass was used as a fertilizer, with the advantage of a straightforward harvesting process. However, more sophisticated technologies for algal harvesting became also increasingly common (e.g. fresh cut from the open sea), especially in Scotland. The potash-enriched liquors obtained from the evaporation of kelp concoctions were used by alum makers with the insoluble residues being valued and used as a fertilizer. Overall, the processing of kelp was very basic, expensive and probably unsuitable for mass production. Yet, due to lack of alternatives it became important with significant production outputs of 5,000 t of kelp from the Hebrides Islands in 1811, at the climax of production (Clow and Clow, 1947). Its decline followed the development of the Leblanc process in 1792 that transformed NaCl into Na₂SO₄ with a series of consecutive reactions. The Leblanc process evolved into the Solvay process in the 19th century (Gillispie, 1957; Thieme, 2002). The focus of these industrial processes remained on the production of glass, soap and paper, thus centering on Na rather than K chemistry. However, a kelp-based industry of commercial value played a vital role in ensuring potash supply to the USA during the years of World War I (WWI) as detailed both in Figure 1 and Section 3.2 (Neushul, 1989).
**Barilla** obtained by burning halophytes plants (e.g. *Salvia soda*) and commercialized especially in Spain and Italy. Halophytes ashes directly incorporated in mixtures of calcia and silica for glass making or lixiviated with water for saponification.

**Kelp** obtained by burning marine algae. Used in Scotland during the 18th and 19th century with algae particularly Na-rich. Sodium was considered favorably by glass and soap makers that sold as *sandalver*.

**Potassium ore** becomes the prominent source of K at the end of the 18th century. **Soluble ores** include sylvinite (KCl), salt peter (KNO3), potash sulphate (K2SO4), potash or perlash (K2CO3), sylvine (KCl•NaCl), camallite (KCl•MgCl2•6H2O), kainite (4KCl•4MgSO4•11H2O), langbeinite (K2SO4•2MgSO4•2H2O) and polyhalite (K2SO4•2CaSO4•MgSO4•2H2O). Other ores include insoluble K-feldspar (KAlSi3O8), alunite (KAl3(SO4)2(OH)6), leucox (KAlSi2O5) and greensand.**Brines** obtained at Searles Lake (California) have also been used as a source of potash in the period between WWI and WWII.

**Figure 1 Timeline of the development of potash sources**
2.2. The American wood ash industry

Before independence from England (16th-18th century) the production of wood ashes in the American colonies was significant with potash being by far the main chemical product and an important source of income in developing economies such as the early settlement of Massachusetts (Garrett, 1996; Kreps, 1931. Roberts, 1972). The Atlantic coast provided favorable logistics for potash trades. However, differences existed between the northern colonies that could take advantage of both skilled workers and high quality raw material, and the southern colonies that lacked both. Overall, the full development of the potash industry in the American colonies may have been delayed with respect to its actual potential, mainly because of technological factors (Roberts, 1972). At the beginning of the 18th century the major obstacle for the American producers was the heavy duty imposed by England. This was removed in 1751, in order to satisfy internal demand in England that could not be met anymore due to worsening of the relationships with Russia (Browne, 1926; Kreps, 1931). This decision had a crucial role in promoting technical advances in the Americas, and yet potash production was still costly by the 1750s. Thus, despite supplementary incentives from the local colonial administration to promote both manufacture and export, the potash industry remained of minor relevance (Kreps, 1931). The forthcoming success of the industry at the beginning of the 19th century can be attributed to the technological improvements of the early processes that made the large-scale production of wood ash economically sound (Kreps, 1931; Roberts, 1972). In turn, this improvement came from the interplay of: i) transportation costs to/from the frontiers of the territories, ii) cold winters and iii) presence of potash-rich raw material (forest trees). The migration of the potash industry towards the West followed more or less the migration of the frontiers. Ultimately, such migration was determined by the need to clear forests to make farming possible and not by an increased demand for K. With the expansion of the territories the cost of transportation increased and the trade of ashes obtained as a byproduct of deforestation provided an efficient means to amortize it. This was especially true during the winters of the northern territories, when significant amounts of ashes were produced as a byproduct of household heating.

In 1788, more than 30 years after the English taxation was eased, technological breakthroughs led to a flourishing industry; for example, 250 potash-works were operating just in Massachusetts. In 1790, almost immediately after independence, the first patent granted by the newly formed USA government was issued to Samuel Hopkins for a process to improve the release of potassium from wood ashes, clearly indicating the critical role of the potash sector (Kreps, 1931; Maxey, 1998a; Maxey, 1998b). Years later, in 1808, as a consequence of the Napoleonic wars the price of potash tripled (Browne, 1926; Miller, 1980). Under these favorable economic circumstances for the American producers massive exports towards Europe began without government assistance. There is evidence that the independent variable in this early potash market was demand (Kreps, 1931). By the end of the Napoleonic wars a new series of concomitant factors transformed the life of the backwoodsman (Darst, 1991; Garrett, 1996; Hager, 2008; Kreps, 1931; Neushul, 1989): i) lumber became scarce on the Atlantic coast with the frontier of settlers moving westward; ii) crude forms of potash lost their competitiveness in the British market with respect to pure and cheaper sodium salts obtained from the Leblanc process (Gillispie, 1957; Thieme, 2002); iii) important sources of sodium and potassium nitrates were discovered in the Atacama desert of Chile; iv) the development of the railway made the trade of lumber and agricultural products more lucrative than that of ashes, especially after the repeal of the English Corn Laws, and v) Canada (one of the biggest importers of American ashes) was in the process of establishing its own potash industry. Revenues from potash exports fell back from the psychological threshold of US$1 million by the 1830s,
indicating the beginning of the decline of the American potash industry from wood ashes. From the standpoint of the upcoming agricultural needs of the United States in the 19th-20th century, Browne used the expression **economic crime** to describe the decline of the early industry (Browne, 1926). He argues that when potash became appreciated for its fertilizing properties, its manufacturing had already disappeared in the USA and that almost two centuries of potash exports towards Europe impoverished American soils impeding agricultural development in the eastern United States (Browne, 1926).

Although there are few commonalities between the diversity of developing countries in the modern world and the British Empire of the 18th century, we observe that two macro-system conditions seem to recur in the potash market: high demand and monopolized production that force some countries to depend on foreign imports. The Scottish experience demonstrates that exports to other countries might remain advantageous until an adverse condition occurs (e.g. prices spike or discontinued supply), whereas the American experience demonstrates two different aspects. During the 18th century a robust and cost-effective technology was necessary to establish a proper potash sector. Without such technology and even in presence of other favorable economic conditions (e.g. low taxation regime), the industry would not have survived. However, during the 19th century emerged a different picture, with production influenced by the economic rationales of cost savings, offer and demand rather than technological problems. The American experience shows the failing of short-sighted economics that focused on the exploitation of the resources available in a specific moment, without considering the availability of supplies over the long term.

### 2.3. The German potash mining industry

Among the first references on the use of minerals as plant nutrients is the work of J. R. Glauber (16th century) (Darst, 1991). However, it was not until the 18th century that geological sources were adopted as fertilizers. Building on the early work of Karl Sprengel (1787-1859), Justus von Liebig (1803-1873) established that inorganic compounds and mineral sources could be used as a source of nutrients vital to plants and crops (Brock, 2002; Darst, 1991; De'sigmond, 1935; Lodge, 1938; Russel and Williams, 1977; Smil, 2004; Ulrich and Frossard, 2014; van der Ploeg et al., 1999). Their work was further complemented by the research of John B. Lawes (1814-1900) (Leonardos et al., 1987; Lodge, 1938; Russel and Williams, 1977; Ulrich and Frossard, 2014). With this new understanding, the old method of ash lixiviation was abandoned and the idea of mining potassium minerals became prominent. Potash mining had the clear advantage of being implementable on very large industrial scales, a concept acclaimed by the tycoons of the industrial revolution. Furthermore, the high K₂O content in the final product allowed a significant reduction in transportation cost. Germany had extensive potash deposits formed during the Upper Permian, from the Zechstein Sea which was present in an area that now corresponds to a wide area of Central Europe (UK-Poland). Given a tradition of collaboration between government, academia and industry, Germany was an ideal location to test out the use of potassium minerals as fertilizers. Indeed, some of the driving forces behind the establishment of the potash industry can be attributed to the interventions exerted by the Prussian government as well as in the work of German scientists who were interested in the cultivation of potassium-demanding crops such as sugar beets (for the production of sucrose) or potatoes (as a staple food). The Permian Zechstein deposits were properly explored by 1843 and about 20 years later, in 1861 they became commercially available in Stassfurt, mainly due to the work of Adolph Frank
(1834-1916) (Frank, 1893; Noyes, 1966; Russe l and Williams, 1977; Tosdal, 1913). It was the turning-point in the history of potash.

Almost immediately, the ash market for glass and soap production was transformed into a global mining enterprise that targeted the agricultural sector. With a virtually complete monopoly, Germany became the world center of potash trade and remained so for about a century. In the USA, with the completion of all major geographical exploration, further expansion of agricultural land became impossible pushing towards yield intensification. The relatively concentrated potash supplied by Germany became an unbeatable product that was unique among globally traded commodities, and no viable economic alternative to the exploitation of the German mines was possible (Figure 1, Figure 2). As in the USA, the ashes industry disappeared from the rest of Europe (Östlund et al., 1998). As a consequence, until about 1910 the world trade of potash was controlled by businessmen on both sides of the Atlantic, Germany exporting and the USA importing. These trading relationships were seriously strained by the advent of WWI.

3. THE EARLY 20th CENTURY: 1910-1930

Ambition for large profits led to intense competition but also cartelization and overcapacity of the potash sector. The unhealthy status of the potash industry and the complete dependency on potash supplies from the German Kalisyndicate became evident at the beginning of the 20th century. In 1910, the German government approved the potassium law, banning any exports outside the national border (Anonymous, 1911a; Kreps, 1931; Mohme, 1929; Tosdal, 1913). After years of successful business, the USA faced a problematic situation (Supplementary Material). Most European countries faced a similar crisis although some specific distinctions can be made (Dolbear, 1915; Holmes, 1919):
i) Potash deposits were discovered in Catalonia, Spain in 1912 (Gale, 1919b). Although the production was thought to be useful only for the internal market, German producers understood the strategic value of these deposits and secured control over a good portion of them. The counteraction from the Spanish government was to approve a set of laws that, in their essence, required a) constant operation of the deposits by anyone granted mining privileges, b) concession of mining rights owned exclusively by the government and c) protectionist measures to favor internal consumption (e.g. export control). Overall, this government intervention hindered the development of the potash sector, discouraging the flow of capital originating from foreign countries and investors, but successfully granted potash independence for Spain (Dolbear, 1915).

ii) Potash deposits were discovered in 1869 in Alsace and experienced an accelerated development in 1903. The waterways of the Rhine were advantageous for the Alsace mines that produced ore with an average K₂O grade of about 22 wt %. (Gale, 1920). In 1919, production was about 400 t/day (Gale, 1920). Under the French administration, the purchase of three German companies in receivership was authorized and in 1924 the victory of the Gauche (left wing) in the French parliamentary elections favored the nationalization of the mines. Thus, if in 1913 about 58,000 t of pure potash were extracted by 1925 the number soared to 300,000 t (Mohme, 1929; Shreve, 1927). The newly-formed German-French cartel controlled almost the totality of the USA market with a 70/30 share ratio. The same division, more or less, applied to other global trades (Shreve, 1927). The Alsatian mines have remained in operation for several years but since the 1980s the economically-accessible potash-rich seams have been exhausted.

iii) Great Britain had a considerable interest in breaking dependency on imports from Germany. Attention focused on feldspar and recovery of K from cement and steel production flue gases (Holmes, 1919). Ashcroft (1917; 1918) re-proposed the idea developed by Basset in 1913 (Bassett, 1913a), which was to use a high temperature treatment on a mixture of feldspar and NaCl. However, the feldspar deposits suggested by Ashcroft (1917) are remote, located in the far NW of Scotland, and no commercial success was obtained.

iv) At the end of WWI Norway established a Raw Materials Laboratory, where V. M. Goldschmidt (1888-1947) was employed (Mason, 1992). Pioneering experiments were conducted on the production of phosphate fertilizers from apatite-bearing carbonatite rocks, and the use of micas, especially biotite, and K-feldspar as sources of K (Goldschmidt, 1922). Goldschmidt and Johnsen (1922) were the first to show that biotite is the dominant source of K for plants where these minerals occurred in soils in northern Europe, and Cranner (1922) demonstrated the efficacy of micas as sources of K for plant growth. In collaboration with the Agricultural College of Norway, the Norwegian Geological Survey carried out experiments lasting up to 9 years demonstrating that silicate minerals can be beneficial in peaty soils (Retvedt, 1938; Solberg, 1928).

v) Elsewhere in the world minor production emerged from Poland and the Middle East (particularly in Palestine) although collaboration with the Franco-German cartel was necessary for these countries to succeed (Mohme, 1929; Smith, 1936). China and Russia were experiencing their respective communist revolutions and became major players in the potash market starting from the 1950s. Chile played a very important role in shaping the mineral fertilizers market, first, because of the war for the control of guano and second because of the Na (and K) nitrate deposits in the Atacama Desert (Hager, 2008; Holmes, 1919; Smil, 2004). Brazil, which by virtue of its demand has a fundamental role in the modern potash market, had only a minor opportunity to develop its own potash mines in Sergipe, only after the end of World War II (WWII). Canada was an
important distribution center of wood ashes during the 19th century. However, like Russia, it properly
developed its potash industry decades later (Anderson, 1985; Hart, 1912; Kreps, 1931; Miller, 1980).

For the USA the hope of eroding part of the Franco-German cartel was little, unless local potash sources could
be found as leverage. Two main solutions were proposed: exploration for local deposits and investigation of
alternative potash sources (Dolbear, 1915; Hart, 1915; Howe, 1913; Meade, 1917; Stockett, 1918; Teeple, 1921;
Turrentine and Shoaff, 1919). Mineral exploration began in 1911 (Anonymous, 1911b; Stockett, 1918;
Turrentine, 1942). The following potash deposits were discovered: Sandhills, Nebraska (1912) (Jensen, 1987);
Permian basin of Texas (1912; core not drilled until 1926) (Mansfield, 1923; Turrentine, 1938); Searles Lake,
California (1913; operating since 1870s as a borax producer) (Mumford, 1938); Carlsbad, New Mexico (1926;
commercial in 1931) (Cramer, 1938; Garrett, 1996; Jacob, 1958; Turrentine, 1942; Turrentine, 1943). The history
of mineral exploration is well documented (Cramer, 1938; Garrett, 1996; Jensen, 1987; Mansfield, 1923;
Mumford, 1938; Noyes, 1966; Turrentine, 1938; Turrentine, 1942; Turrentine, 1943). A second chapter of
interest for the present world situation is that related to the sources of potash considered and investigated by
American scientists. Here, we focus on four specific cases: i) the brine industry of Nebraska ii) the kelp industry
of California, iii) production of potash from silicate minerals, and iv) production of potash from non-conventional
sources (e.g. distillery residues or cement-kiln flue dusts).

3.1. The Nebraskan brine industry

The short-lived production from brine in Nebraska is the very first attempt to establish an independent potash
sector in the USA. Alkaline crusts from the western Sandhills area were known as early as 1900 (Gosselin et al.,
1994; Hicks, 1921; Jensen, 1987). Brines were known and exploited elsewhere in the USA, including Salduro,
Utah and, most notably, in Searles Lake, California (Hayes, 1942; Teeple, 1921). The Nebraskan industry started
in 1912 from private initiative (Jensen, 1987). Although a railroad was situated in the vicinity of the processing
facilities, production costs alone exceeded the selling price and by 1913 the plant was shut down (Jensen, 1987).

One year later, with the worsening of the political crisis in Europe and the first signs of potash shortages, the Nebraskan production was resumed (Figure 3). Technical improvements were implemented and by 1917 the Potash Reduction Company was producing profitably about 7 t of K₂O/day (Jensen, 1987). With the extreme shortage of overseas potash during the years of the war, many other plants appeared throughout the salty lakes region of Nebraska. There are records of 10 plants capable of producing 100 t K₂O/day or more (Jensen, 1987).

The potash bubble attracted further investors, despite the evident limitation that such business success was tied to the embargo on imports from Germany. By 1920 the main concerns were that the alkaline wetlands were too low in potash salts to ensure a stable profit. There was a strong intention from the State Governor Samuel McKelvie to have federal legislation passed to impose an import duty on foreign potash, so that the local industry could remain competitive. However, the cotton-farming lobby in need of huge quantities of affordable potash had more influence: between 1920 and 1921 potash was again imported from Germany and all the plants in Nebraska shut down. Together with Nebraska, the other major source of potash from brines was located at Searles Lake in California. Here early difficulties were encountered due to the complex chemical composition of the brines that led to a difficult and costly separation process, despite an average K₂O content of about 7.5 wt % (Gale, 1938; Mumford, 1938; Teeple, 1921). Furthermore, the logistics were not ideal, with the evaporation process and the subsequent refinements taking place in two different locations. Overall, the production of potash in California was successful in the period across the two World Wars but later on had to focus on the production of borax.

3.2. The Californian kelp industry

Concomitant to the Nebraskan development is the potash industry from kelp in California (Neushul, 1989). An advantage of this development was that the organic matter left over after lixiviation of kelp may have been used as a source of N, for example in fodder (Cameron, 1912). The main limitations were instead that the states of the Pacific Coast and Hawaii, where kelp could be harvested, consumed less than 2% of potash whereas more than 90% was consumed East of the Mississippi river (Stockett, 1918). Kelp was being investigated as an industrial source of potash as early as 1913 and a proper commercial development began in 1914 (Howe, 1913; Merz and Lindemuth, 1913). Encouraging publications from government surveys led to eleven companies being formed by 1916. By 1917 kelp was the second source of potash supply in the USA, with the Nebraskan and Californian brines being the first (Cameron, 1915; Neushul, 1989; Stockett, 1918). In the same year, an experimental station for the study of kelp processing was established in Summerland, under the management of J.W. Turrentine (Howe, 1913; GC Spencer, 1920; G.C. Spencer, 1920; Tanner, 1922; Turrentine and Tanner, 1922; Turrentine et al., 1923; Turrentine and Shoaff, 1919; Turrentine and Shoaff, 1921) and aided by massive public investments, probably drawing from the earlier relative success of the Scottish industry and because of the pressing need of the USA to become self-sufficient. As a matter of fact, this was the only substantial potash project under government development (Turrentine and Shoaff, 1919). Due to the research of Chaim Weizmann (1874-1952), industrial fermentation was about to become a reality. Kelp fermentation for the production of acetone became a large-scale success in 1916. Potash was a valuable byproduct. The process was implemented by the Hercules Powder Company, as acetone was extensively used in the production of cordite, an explosive that was necessary to the British armed forces. Overall, during the 1910s 24,000 t of kelp were harvested per month and revenues of about US$345 million (2014 equivalent value) were obtained at the peak of success (Neushul, 1989) (Figure 4a). The economic sustainability of the process was confronted with the end of WWI that caused
the market for explosives to shrink. The fermentation process lost its competitiveness against mineral sources of K that once again were being marketed under the supervision of the new Franco-German cartel. In this new situation the potash kelp industry disappeared. However, the industrial knowledge gained from that experience found new applications in the late 1930s for the production of hydrocolloids such as alginates and carrageenan.


The Californian kelp industry reached significant industrial output within a very short period of time. It was aided by both private and public investments. However, as had happened earlier in the history of potash manufacturing, investments alone did not suffice to develop a proper sector. A relatively high-cost technology coupled with seasonal variation in the amount of kelp harvested could be offset only when lucrative alternative markets for the byproducts were available. Thus, the Californian kelp industry is a reminder of the necessity for initial investments, affordable technologies and sensible economic planning.

3.3. Production of potash from silicate minerals

During WWI, K-bearing mineral sources alternative to standard soluble ores were considered promising by several authors. The first work on potash-rich silicate rocks as source of potassium led to a patent in 1847 by Tilghmann (Ross, 1913; Tilghman, 1847). The process was based on the grinding of a K-rich feldspar with calcium carbonate and calcium sulphate and heating to redness for 8 hours. An alternative treatment with NaCl was also proposed in the same patent. The release of potassium from silicate rocks is a soil-forming process that occurs at a particularly low rate (Supplementary Material). Thus, treatment was deemed necessary to effectively improve the release of K from the silicate matrix. Overall, the processing proposed during the 18th and 19th centuries comprised two sub-categories: i) wet and ii) dry (high temperature) treatments. The former mainly centered on the use of hydrofluoric acid (HF). The latter centered on attempts to liberate potassium via formation of amorphous and/or new solid-state phases (Cushman and Coggeshall, 1912; Cushman and Hubbard, 1908; Ross, 1913; Ross, 1917; Spiller, 1882). This second approach was probably the logical consequence of applying treatments similar to the analytical method of Lawrence Smith (Hart, 1915; Smith, 1871). In 1918 Buck published
an updated bibliography of the treatments that had been proposed (Buck, 1918). A selected overview of patented technologies to extract potash from K-feldspar is presented in Table 1. Overall, these patents demonstrate limited knowledge of materials science and lack of thermodynamic data in the early 20th century. Manning discussed the value of untreated K-bearing silicate minerals in the modern potash context (Manning, 2010; Manning, 2012), and recently patented technology demonstrates a new interest for this sector (Ladeira, 2013; Yasuda and Warwick, 2013).

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PROCESS</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet chemistry</td>
<td>KFS+(Na)K₂CO₃(or (Na)KOH)+T+P (see original)</td>
<td>(Frederick C. Gillen, 1917)</td>
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<tr>
<td></td>
<td>KFS+CaCO₃+T+P</td>
<td>(Andrews, 1919)</td>
</tr>
<tr>
<td></td>
<td>KFS+CaF₂+H₂SO₄+T</td>
<td>(Foote and Scholes, 1912)</td>
</tr>
<tr>
<td></td>
<td>KFS+borax+(Na)K₂CO₃(or (Na)KOH)+T+P</td>
<td>(William H. Gillen, 1917)</td>
</tr>
<tr>
<td></td>
<td>KFS+HF (electrolysis)</td>
<td>(Cushman, 1907)</td>
</tr>
<tr>
<td>Dry chemistry</td>
<td>KFS+NaCl</td>
<td>(Bassett, 1913a)</td>
</tr>
<tr>
<td></td>
<td>KFS+NaCl+Na₂CO₃</td>
<td>(Bassett, 1914b)</td>
</tr>
<tr>
<td></td>
<td>KFS+NaCl+CaCO₃</td>
<td>(Rhodin, 1900a; Rhodin, 1900b)</td>
</tr>
<tr>
<td></td>
<td>KFS+NaCl(or CaCl₂)+CaSO₄</td>
<td>(Morse and Sargent, 1912)</td>
</tr>
<tr>
<td></td>
<td>KFS+NaNO₃</td>
<td>(Blumenberg, 1919)</td>
</tr>
<tr>
<td></td>
<td>KFS+Na₂SO₄+Na₂CO₃</td>
<td>(Bassett, 1913b)</td>
</tr>
<tr>
<td></td>
<td>KFS+(K)NaCl+(K)NaH₄SO₄</td>
<td>(Thompson, 1911)</td>
</tr>
<tr>
<td></td>
<td>KFS+(K)NaCl+(K)NaH₂SO₄+C</td>
<td>(Bassett, 1914a)</td>
</tr>
<tr>
<td></td>
<td>KFS+soda ash (vitrification)</td>
<td>(Vanderburgh, 1864)</td>
</tr>
<tr>
<td></td>
<td>KFS+(K)Na₂O (see original)</td>
<td>(Rody, 1919)</td>
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<tr>
<td></td>
<td>KFS+(Na)K₂SO₄+C</td>
<td>(Hart, 1913)</td>
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<tr>
<td></td>
<td>KFS+(Na)K₂CO₃+H₂O(g)+P</td>
<td>(Samuel Peacock, 1912b)</td>
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<tr>
<td></td>
<td>KFS+K₂SO₄(or KHSO₄)+SO₂</td>
<td>(Neil, 1912)</td>
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<tr>
<td></td>
<td>KFS+CaO+vapour</td>
<td>(Pohl, 1910)</td>
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<td></td>
<td>KFS+Ca(OH)₂+P</td>
<td>(Gibbs, 1909)</td>
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<td></td>
<td>KFS+CaO+phosphate rock</td>
<td>(Benjamin Peacock, 1912)</td>
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<td></td>
<td>KFS+CaSO₄+C</td>
<td>(Swayne, 1905)</td>
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<tr>
<td></td>
<td>KFS+(Na)K₂CO₃(or (Na)KOH) (see original)</td>
<td>(Frederick C. Gillen, 1917)</td>
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<tr>
<td></td>
<td>KFS+CaCO₃</td>
<td>(Samuel Peacock, 1912a)</td>
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<td></td>
<td>KFS+CaCO₃</td>
<td>(Brenner and Scholes, 1920)</td>
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<td></td>
<td>KFS+CaCO₃+acid sludge</td>
<td>(Blumenberg, 1918)</td>
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<td></td>
<td>KFS+CaCO₃ (cement making)</td>
<td>(Spencer, 1915)</td>
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<td></td>
<td>KFS+Ca₃(PO₄)₂</td>
<td>(Haff, 1912)</td>
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<tr>
<td></td>
<td>KFS+CaCO₃(or Ca(OH)₂)+CaF₂+Ca₃(PO₄)₂</td>
<td>(Klett, 1865)</td>
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<tr>
<td></td>
<td>KFS+NaCl+Ca(OH)₂</td>
<td>(Edwards, 1919)</td>
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<tr>
<td></td>
<td>KFS+Ca₃(PO₄)₂+CaCO₃</td>
<td>(Bicknell, 1856)</td>
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<tr>
<td></td>
<td>KFS+CaF₂</td>
<td>(Mckirahan, 1921)</td>
</tr>
<tr>
<td></td>
<td>KFS+CaCl₂(or NaCl)+Fe (or Fe₂O₄)</td>
<td>(Glaeser, 1921)</td>
</tr>
<tr>
<td></td>
<td>KFS+CaCl₂+MgCl₂</td>
<td>(Dyson and Grimshaw, 1979)</td>
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<tr>
<td></td>
<td>KFS+CaCl₂+CaO</td>
<td>(Blackmore, 1894)</td>
</tr>
<tr>
<td></td>
<td>KFS+CaCl₂+CaO</td>
<td>(Cushman, 1911)</td>
</tr>
<tr>
<td></td>
<td>KFS+CaCl₂+CaCO₃(or MgCO₃)</td>
<td>(Brown, 1915)</td>
</tr>
<tr>
<td></td>
<td>KFS+CaSO₄ (or BaSO₄ or SrSO₄)+CaCO₃</td>
<td>(Thilghman, 1847)</td>
</tr>
<tr>
<td></td>
<td>KFS+BaSO₄+C</td>
<td>(Hart, 1911)</td>
</tr>
</tbody>
</table>
Historically, there are few records of successful businesses based on the mining of silicate sources (for example leucite in Wyoming; Figure 4b) (Hornsey, 1918; Stockett, 1918; Teeple, 1921; Turrentine, 1924). Other sporadic attempts have been made to extract potassium from greensand (glaucnite) in New Jersey (Cameron, 1912; Charlton, 1918; Gale, 1919a; Stockett, 1918; Teeple, 1921; Turrentine, 1924; Van Straaten, 2002). In 1901 Rhodin mentions the proposed establishment of a factory for the processing of feldspar in Stockholm, Sweden (Rhodin, 1901). However, no additional information could be found on this example. The main problem for this type of technology was to find a value for the byproduct. Unless pure alumina and silica could be obtained and sold, potash alone was not enough to recover the cost of either wet or high temperature processing (see Inset).

### 3.4. Production of potash from other sources

At the end of WWI, the main sources of potash in the USA were the Californian brines (Teeple, 1921). However, the potash famine during the war forced researchers to look for imaginative solutions. Thus, there exists a relatively extensive literature concerned with potash production from alternative sources (see Inset). For example, in 1912 it was reported that the city of Cleveland, Ohio, produced potash from waste incineration through a steam-heating process (Cameron, 1912). Ash-based methods developed between the 17th and 18th centuries were never completely abandoned (Figure 1). As an example, production from wood ashes was still operative in Michigan (Kreps, 1931; Teeple, 1921). In Caucasus, potash was obtained from mineral sources but also from the ashes of sunflower stalks (Dolbear, 1915; Holmes, 1919; Mohme, 1929). Ashes are still used in some traditional contexts and their use is debated in the field of waste and biomass incineration (see Inset).

Shales, containing potassium-bearing clays, are one of the raw materials of the cement industry, and fly ashes and flue dusts obtained from cement factories can be rich in K₂O. Cement dusts as a source of potash are mentioned and discussed by several authors (Anderson and Freeman, 1920; Ellis, 1916; Frederick, 1916; Freeman, 1922; Gale, 1919a; Hart, 1915; Holmes, 1919; Huber and Reath, 1917; Jackson, 1922; Kreps, 1931; Meade, 1917; Merz and Ross, 1919; Mohme, 1929; Ross and Merz, 1922; Ross et al., 1917; Shreve, 1927; Spackman and Conwell, 1916; Stockett, 1918). A detailed account of the cement manufacturing companies operating at the close of WWI has been given by Maede (Meade, 1917). Overall the potash industry associated with cement production found a minor success. As an example, in the USA there were at least two plants (one operative up to 1963 and one up to 1970) that sold an agricultural lime made from flue dust. There are examples of the recovery of cement dust in Australia (1945-1951), Sweden, where until 1964 some cement dust was pelletized and sold as a low grade fertilizer, and Finland, where until 1974 similar operations were conducted (Garrett, 1996). Another important source of potash was the waste waters of alcohol distilleries (stillage) and sugar beet factories, accounting for about 6% of the total American production during the 1930s (Gale, 1919a).

This was the result of the work of Dubrunfaut (1797-1881) about a century earlier, who first demonstrated the extraction of potassium carbonate from sugar beet residues (Kreps, 1931). The United States Industrial Alcohol Company became the second largest producer of potash in the USA in 1931. As for the cement industry the main reason for this success was partly due to the public pressure towards the elimination of harmful wastes (Kreps, 1931; Meade, 1917).
The production of ashes still takes place. As an example, incineration of urban wastes is a topical global problem and often encounters a strong opposition of environmental movements and public opinion. Ashes obtained by incineration contain a certain amount of K and other beneficial elements but they can also be a source of pollutants, making them unacceptable to regulators (James et al., 2012; Lam et al., 2010; Zhang et al., 2002a; Zhang et al., 2002b). The development of a proper technology could lead to poison-free ashes to be commercialized as a fertilizer. In contexts other than that of potash, biomass incineration is considered a source of clean energy. Estimations limited to the major producers suggest outputs in the order of 10^16 t/year of ashes obtained by wood residues and an additional 10^15 t/year from wood fuel combustion (James et al., 2012). A recent study on the chemical composition of the ashes of halophyte plants from various origins has shown for some samples K_2O content in the dry plant that are comparable with the content of common K-bearing silicates (Tite et al., 2006). Although it is evident that massive importers of potash such as Brazil would not be able to meet their K_2O demand from ashes obtained by burning such shrubs or other biomasses, these might still be sufficient to provide potash self-sufficiency in smaller settings.

Kelp is a term that has been loosely applied to various species of algae (or algal ashes). The attractive feature of algae is that often they have a higher amount of K than Na, despite the latter being ten times more concentrated in seawater (A.A.V.V., 1981; Cameron, 1915; Chapman and Chapman, 1980; Dolbear, 1915; Vinogradov, 1953). As an example, the ashes of *Nereocystis luetkeana* account for 50.57 wt % of the mass of the dry algae and contain 36.90 wt % of K_2O and 14.12 wt % of Na_2O (Vinogradov, 1953). Both scholars and industrialists have been skeptical on the possibility to reinstate a kelp-based potash industry, despite the consolidated technology for the harvesting of algae. Essentially, this is because the global potash demand will not be met by any of the processing methods available. Here, we want to point out that given the body of knowledge on algae and the prosperity of their market (Boney, 1965), new synergies between algae producers and farmers may be sought. Ireland, Norway, France and UK together with several other countries in Asia continue to produce profitably kelp. In 2009, the alginate industry largely based on algae harvest was worth US$318 million (Bixler and Porse, 2011). Niche industries that commercialize seaweed fertilizers and kelp meals already exist. Although an intensive agriculture cannot rely on these products, local coastal communities could benefit from investigating such opportunity.

Silicate minerals such as K-feldspar are an attractive alternative to soluble ores. China, Italy and Turkey are the major current producers of feldspar but mining activities occur in more than 50 countries. Practically unlimited sources, worldwide availability (50% of all igneous rocks contain feldspars (Barth, 1962)), and slow rate of K-release are advantageous characteristics of K-bearing silicates. The problem is that the weathering rate is likely to be too slow, and/or the cost of processing to increase the rate too high. This cost could be offset if silica and alumina could be obtained as byproducts. However, as demonstrated in the reviews...
Since then, published more than thirty years apart by Noyes (Noyes, 1966) and Rao (Rao et al., 1998) no successes have been reported on that matter. With such resources however, one can only advocate for new avenues to approach this problem. Generally, the question asked is how to improve the extraction capacity, efficiency and logistic of mining operations. Equally important is how to release K from its parenting minerals at a rate that is suitable for crop cultivation. Thus, the commercial failure of enterprises of the past can be overcome if ways to release K at controlled rates are found. In this new perspective the value of silicate minerals become evident.

Currently, there are no cost-effective technologies to quantitatively recover K from seawater. As in the case of the potash rich effluents found in distilleries, sugar beet factories and vinasses from the wine industry, the concentration of potassium is relatively high, but still too low to find applications in the fertilizer industry. Promising developments to concentrate potash from these sources could stem from research on affordable processes based on ion selective membranes and ion-exchangers (España-Gamboa et al., 2011; Sheehan and Greenfield, 1980; Wilkie et al., 2000; Yuan et al., 2012; Zhang et al., 2012).

Lastly, mention must be made to the successes encountered in the use of human and animal excreta as fertilizer. Organic farmers have used manures as a source of K (Fortune et al., 2004), but the quantities available are insufficient for widespread use in agriculture. However, promising developments from this sector might be expected in those isolated communities of the developing world (Cordell et al., 2009; Öborn et al., 2005; Richert et al., 2010).

4. The mid 20th Century: 1930-1950

In the USA, the main concern that arose during the 1920s was to effectively develop a local potash industry after the threat of starvation experienced during WWI. The fear during this period was that Germany would have used its mines to produce potash beyond any real demand, in order to keep the price low. The consequence of such a policy would have been a net cash flow from the USA to Germany, to purchase cheap potash. This situation in turn would have prevented a truly free market and the possibility of investment in a local American potash industry (Meade, 1917). However, early expenditure on geological exploration led to the establishment of a relatively strong mining sector and by 1929, the USA had its own potash producer: American Potash and Chemical. The publication by Turrentine in 1932 terminates the decade of episodes that followed the end of WWI. Much of the research of that period can be found in the publications of the American Potash Institute that was founded in 1935 (later in 1977 the Potash & Phosphate Institute and in 2007 the International Plant Nutrition Institute) (Smith, 1936; Turrentine, 1938; Turrentine, 1942; Turrentine, 1944). At the dawn of WWII, the American potash situation was changed with respect to 30 years earlier. Domestic mining of sylvinitie and langbeinite provided a reliable source of potash and by 1942 imports had fallen to a negligible amount (Hayes, 1942).

5. After World War II: 1950-2000

The destruction brought by WWII effectively broke up the pre-existing potash cartels. On opposite fronts, France and Germany were devastated. The newly formed Soviet bloc became a political superpower and with it, a potash industry was founded to exploit large deposits of potash in the Ural Mountains and in Belarus. In this post-war context Canada discovered the largest potash deposits ever known in the state of Saskatchewan, with commercial operation starting in 1962 (Anderson, 1985). In the UK, Zechstein potash deposits were discovered in 1939, leading to the development of one of the deepest mines in Europe in 1969 (Woods, 1979). Since then,
the potash market had found new patrons: Canada on one side and the Soviet Union (now Russia) on the other. Canadian sources became the major way to obtain potash in the USA, although production continued or was further developed in New Mexico, Utah and Michigan. The research performed only a couple of decades earlier on the processing of silicate minerals (Table 1) became neglected. New international bodies also emerged such as the International Potash Institute (IPI), the International Fertilizer Association (IFA) and The Fertilizer Institute (TFI). The German deposits were split between East and West and entered in a phase of stable production far from the Canadian tonnage but still important on the global scale. Germany is currently the fourth largest producer of potash and the leading supplier in Europe. Over the last 70 years new potash producers and consumers have emerged, new markets have been created and new deposits have been explored (e.g. Danakil region of northern Ethiopia and Khorat Plateau of northeastern Thailand) (Adhia, 1980; Hite and Japakasetr, 1979; Holwerda and Hutchinson, 1968; Piazzese, 1987; Saurat, 1989). The overall development of the global potash industry in the context post WWII has been analyzed among others by Garret, who discusses also some of the chronic problems of the potash sectors (Darst, 1991; Garrett, 1996; Rittenhouse, 1979). First, early deposits were mined regardless the mineralogy and/or grade of the ores. This in turn led to mining sites being opened even by single individuals in their own properties without selection of logistics and/or other economic criteria (Kreps, 1931). Overproduction followed, that not necessarily corresponded to real demand. The classic example is given by operations performed in the planned economy of the Soviet Union where the government expanded the potash sector without control, taking advantage of the forced use of internal artificial markets that made capital and operating costs unimportant (Rittenhouse, 1979). Similar practices, although less extreme, were conducted all over the world with the only true private enterprises in the USA, the UK and some Canadian plants (Adhia, 1980; The New York Times Editorial Board, 2013; Lodge, 1938; Piazzese, 1987). Second, with the exception of Israel, the potash sector did not rely on research and development but rather on an old scheme of industrial processing (Garrett, 1996).

6. Toward the 21st century: a New Global Need

In the future, the need for K can only become greater as population increases, with the greatest demand from regions where, due to the historical development of the global potash industry, indigenous sources of conventional K are yet to be found and developed, e.g. in Africa or South America. Exploration and conventional deep mining of potash salts is a major capital investment, and historical records show that its development can be very slow. Although privatization has occurred over the past 30 years, the constant intervention of governments in the potash extraction sector poses important and complex questions (Rittenhouse, 1979). As long as a high price is needed to justify the financing of new mine projects, it is unlikely that private entrepreneurship will succeed in fully meeting demand through the exploration and opening of new potash mines in the Global South.

However, a new paradigm is emerging, which recognizes the need of new technologies and materials in the potash sector. It starts from the realization that conventional soluble K fertilizers might not be as effective in deep-leached soils as they are in the soils of the northern hemisphere (Leonardos et al., 1987, Leonardos et al., 2000). The similar need for affordable sources of K drove innovation in North America and Europe during the 20th Century, and is expected to propel innovation for the Global South in the 21st Century.
7. CONCLUSION

The historical focus of this study shows that the current potash market has been shaped by i) the development, following Von Liebig, of soluble chemical fertilizers and ii) the economic and political support provided by governments of northern hemisphere countries. Current conventional chemical fertilizers are designed for use in slowly-weathered, often poorly drained, soils of the northern hemisphere, in contrast to the requirements of deeply weathered rapidly leached soils that predominate in tropical and subtropical regions. Economic and political support of national potash production took the form of either direct financing or tight market and export control, key elements that made possible and enabled large scale operations of existing salt mines and extraction plants.

In order to sustain crop production proper potassium levels must be maintained in agricultural soils, especially in the Global South where farmers might experience economic barriers and physical barriers in accessing potash. Exploration for conventional new deposits and development of new potash mines shall continue throughout the 21st century in order to ensure potash self-sufficiency to developing countries. However, contrary to the past the heavy burden of initial time and capital investment is unlikely to be supported by government budgets. Thus, a multilocal rather than global potash market could be envisaged, which will consider regional logistics and geopolitical factors. Diversified actions will be required and the elements presented in this paper provide initial guidelines. Technical solutions for the production of potash from local sources have indeed been brought forward throughout history, although few have survived to the commercial success of mining potash salts. In the present global context, it is possible that some of these solutions can answer the needs of our century, particularly when specific geographical conditions and long-term sustainability are considered. The direct consequence of innovation in the potash sector will be the development of efficient and affordable agricultures in the Global South and ultimately the possibility to feed the world.
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SUPPLEMENTARY MATERIAL

Historical and technical developments of potassium resources

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THE POTASSIUM CYCLE

Figure 1 The biogeochemical cycle of potassium. Arrows indicate processes that occur at human time-scale (t/year). Broken arrows indicate processes that occur at geological time-scale (t/million years). The bold dashed arrow emphasizes the mining of potash ores which transfers at a very high rate huge amount of potash from the lithosphere of one side of the world to the soil solution of the other side.

Potassium is an alkaline metallic element found in nature in its oxidation state of +1. It is the seventh most abundant metal on Earth occurring in common silicate minerals such as alkali feldspar (KAlSi₃O₈) and micas (e.g. KAl₂Si₃O₁₀(OH)₂) (Burkhardt, 2002; Haynes et al., 2012). Within rocks known as evaporates it occurs as a number of different salts, including sylvinite, a mixture of KCl and NaCl. Potassium participates in an Earth-scale biogeochemical cycle (Figure 1). Human activities strongly influence the net flux of potassium in some specific parts of the cycle. Potash is added as fertilizers to agricultural soils, and about 30-40 wt % is rapidly leached to enter groundwater or surface water systems. The remaining amount is removed due to three main causes (Figure 1): i) farming ii) grazing and iii) soil processes such as erosion or other biological activities. Thus, the amount of potassium supplied in the soil as a fertilizer must be found in residual biomasses and manure or, alternatively, it must enter into the human diet through fresh consumption, processed food or meat obtained from fodder feeding (Figure 1). K⁺ is a soluble cation and, as such, is scarce in body tissues (0.25 wt %) but abundant in the body fluids (Iyengar et al., 1978). Thus, potassium is continuously uptaken and excreted by human beings, with a total average excretion estimated to be of 1.1 x 10⁻³ t • person⁻¹ • yr⁻¹ with variations depending on the nature of the staple diet (Richert et al., 2010). If a total population of 9.5 billion people is considered, an approximate total amount of potassium of 10⁷ t/year will be excreted by humans, the same order of magnitude of the ore currently mined. This amount is “lost” in either sewage sludge, or in the hydrosphere, or in biological sub-cycles (Figure 1). The greater potassium collectors are the oceans. However, it
has been demonstrated that the low concentration of K in seawater (0.038 wt %) remains more or less constant unless changes in the rate of formation of the oceanic crust occur (Barth, 1962; Hardie, 1996). Locally, higher concentrations of K (up to ≈ 0.6 wt %) can be found in marine organisms such as kelp. This observation correlates well with the long residence time of K in the ocean (≈ 10^7 years) (Barth, 1962; Spaargaren and Ceccaldi, 1984). Formation of evaporites (rocks produced when seawater evaporates) removes potassium from seawater and transfers it to the lithosphere (e.g. fast evaporation that leads to evaporites or sedimentation). Reactions involving clay minerals also remove K from water trapped in sediments (smectite-illite transformation), and as part of the rock cycle these may change during burial and metamorphism, ultimately melting to produce granitic rocks. K-bearing silicate minerals are destined to slow weathering processes that occur at rates in the order of 10^-7 t • m^-2 • yr^-1 (Manning, 2010) (Figure 1).

As long as the cycle follows its geological rhythm, the growth of crops is limited by the potassium naturally available in the soil. Human-driven mining of potash ores allows the soil solution to be replenished in potassium, thus promoting agricultural yields towards new records. However, mining proceeds at a rate (t/year) that is 10^6 times faster than the rate of formation of new potassium minerals (t/million years).
CLASSICAL AND PRE-INDUSTRIAL PRODUCTION OF POTASH

Glasses, ceramics, soaps and gunpowder are products largely dependent on the chemistry of potassium (Burkhardt, 2002; Davy, 1808; Kreps, 1931). References to the manufacturing of potassium salts are found in the Egyptian civilization (3rd millennium BC) (Tite et al., 2002). The Bible mentions the use of lye in the book of Jeremiah (7th-6th centuries BC) (Jeremiah). Glass-making with potash is described by Pliny the Elder (1st century AD) and potash compounds are found in antique Chinese porcelains (Yanyi, 1987). Potash had been obtained from rush ashes by Aristotle (384–322 BC) and from argula ashes by Dioscorides (40-90 AD) (Kreps, 1931).

Traditionally, potassium compounds were made by treating wood ashes with water (lixiviation) followed by concentration of the solution by boiling. To describe this process that occurred in small pots, the word "pot-ash" (later anglicized to potassium) was introduced. In modern times potash production became a much better documented process, mainly due to the increased demand imposed by the industrial revolution and the shift in potash use from the glass and soap industries to large-scale agriculture. Thus, if few quantitative data are known on potash production during ancient periods, more accurate accounts are available starting from the 18th century.

THE POTASH CRISIS DURING WORLD WAR I

As WWI approached, the relationships between the USA and Germany worsened dramatically. Within the USA, an intense debate occurred between 1910 and 1925, and was at times emotional (Anonymous, 1911a; Cushman, 1917; Jensen, 1987; Meade, 1917; Mitchell, 1911; Stockett, 1918; Turrentine, 1942). Potash was quoted at about US$790/t before the war and peaked at US$7,336/t by 1917 (prices are given in the inflation-adjusted 2014 equivalent) (Cushman, 1917). During the fiscal year ending on June 30th 1914, the USA imported 1,066,929 t of potash to be used as fertilizers. During the subsequent six months, July 1st - December 31st 1914, the amount fell to 182,192 t, due to the effects of the German export ban (Dolbear, 1915). In 1916 the domestic product of the USA amounted to less than 9,000 t with an estimated need of more than 300,000 t (Cushman, 1917). The dramatic situation is well captured by the patriotic tones of the short pamphlet published by Mitchell in The National Geographic Magazine (Mitchell, 1911). A further indication of the national feelings of that period is expressed by the words of secretary of commerce Herbert Hoover as quoted by Shreve: “It is our job systematically to build up sources of supply in all these raw materials which are now under monopolies. We must have adequate supplies to free us from these things in the future. The American people can help themselves. They don't have to ask anybody for help” (Shreve, 1927). Years later, with the establishment of a new Franco-German cartel it was again in Hoover’s words that we can perceive all the anger of the American administration on the potash situation: “this is a governmental monopoly of the most vicious order”, that gave Germany “full liberty to milk the rest of the world”. It was a direct accusation of antitrust violation made to the Kalisyndikat. These words also reveal the high level of involvement of public opinion in the potash debate of that time (Stockett, 1918), that was also part of the educational programs of universities and agricultural schools (Bradshaws, 1907; de Turk, 1919; Gallup, 1905; Shreve, 1927; Williams, 2010).
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