



# MIT Open Access Articles

## *Historical and technical developments of potassium resources*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

<b>Citation</b>	Ciceri, Davide, David A.C. Manning, and Antoine Allanore. "Historical and Technical Developments of Potassium Resources." <i>Science of The Total Environment</i> 502 (January 2015): 590–601.
<b>As Published</b>	<a href="http://dx.doi.org/10.1016/j.scitotenv.2014.09.013">http://dx.doi.org/10.1016/j.scitotenv.2014.09.013</a>
<b>Publisher</b>	Elsevier B.V.
<b>Version</b>	Author's final manuscript
<b>Citable link</b>	<a href="http://hdl.handle.net/1721.1/106614">http://hdl.handle.net/1721.1/106614</a>
<b>Terms of Use</b>	Creative Commons Attribution-NonCommercial-NoDerivs License
<b>Detailed Terms</b>	<a href="http://creativecommons.org/licenses/by-nc-nd/4.0/">http://creativecommons.org/licenses/by-nc-nd/4.0/</a>

# Historical and technical developments of potassium resources

Davide Ciceri<sup>a</sup>, David A.C. Manning<sup>b</sup> and Antoine Allanore<sup>c</sup>

<sup>a</sup> Department of Materials Science & Engineering. Room 13-5066 Massachusetts Institute of Technology. 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA. Email: ciceri@mit.edu

<sup>b</sup> School of Civil Engineering and Geosciences Room 3.01 Drummond Building. Newcastle University. Newcastle upon Tyne NE1 7RU, UK. Email: david.manning@ncl.ac.uk

<sup>c</sup> **Corresponding author:** Department of Materials Science & Engineering. Room 13-5066 Massachusetts Institute of Technology. 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA. Email: allanore@mit.edu

## ABSTRACT

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 20<sup>th</sup> 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 'offtake'; 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  $N_2$  from the air and  $H_2$  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 %  $K_2O$ ).

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; Leonardos 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  $K_2O$ , 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

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

14 *Environment* is the third imperative that a sustainable model needs to confront. Current mining activities raise  
15 questions on deterioration of air and water quality as well as landscape modification/degradation (Azapagic,  
16 2004; Dold, 2008; Anonymous, 2001; Russel and Williams, 1977). From a soil perspective the imbalance in offtake  
17 through cropping impoverishes the quality of the soil. However, different situations are observed for the three  
18 main nutrients. N is approximately in balance in the world soils meaning that agronomic inputs (fertilizers plus  
19 manure) equal the outputs (crop harvests; Sheldrick et al., 2002). Similarly, P global inputs exceeded the outputs  
20 in the year 2000, although 30% of the global cropland still experienced a deficit (MacDonald et al., 2011).  
21 Balanced levels of N and P in soils that are subject to through drainage suggest excessive application of fertilizers  
22 that leads to the critical problem of eutrophication of the aquatic ecosystems (Cordell et al., 2009; Frink et al.,  
23 1999). For K, in contrast, deficits have been reported especially for the African continent (Sheldrick and Lingard,  
24 2004) as well as for China and India (Römhild and Kirkby, 2010). Significant reduction in K use has been observed  
25 also in many European countries (Öborn et al., 2005; Somerwill et al., 2012). Low K levels suggest agronomic  
26 practices overly intense with respect to the amount of potash replenished by fertilizers. If potassium deficits are  
27 not corrected, fertility loss will have to be faced. While such correction can be relatively easily implemented in the  
28 northern hemisphere, the deep leached soils of the Global South might be at risk. Furthermore, even if actual  
29 potash fertilizers from the North should reach the South, a high carbon cost for transportation, along with the  
30 effects of salinization and chloride, or loss through drainage, will have to be handled (Bernstein, 1975; Cordell et  
31 al., 2009; Lodge, 1938; Rozema and Flowers, 2008). Alternative approaches have been put forward. For example,  
32 the concept of *agrogeology* proposed as early as 1862 and redefined by van Straaten, aims at fertilizing the soils  
33 of the Global South by using slow nutrient-releasers of geological origin such as unprocessed P- or K- bearing rocks  
34 (*petrofertilizers*) (De'sigmond, 1935; Leonardos et al., 1987; Leonardos et al., 2000; Van Straaten, 2002; Van  
35 Straaten, 2006). Movements such as *Rochagem* have promoted this concept (remineralize.org, 2014).

36 Overall, concerns on the possibility of a sustainable agriculture for the 21<sup>st</sup> century seem justified and the role of  
37 fertilizers appears pivotal. In this paper we focus on K-fertilizers. The sustainability challenge is to develop a  
38 potash market that takes into account affordability, local availability and compatibility with crops and soil  
39 composition (Van Straaten, 2006). To achieve this market, it is essential to understand the historical and social  
40 context (Cordell et al., 2009; Scholtz and Wellmer, 2013; Ulrich and Frossard, 2014) that has led to the present-  
41 day situation. Therefore, this paper addresses the history of potash production from 1700 to the present on the  
42 basis of several multidisciplinary sources. The intimate interconnections between geopolitical, economic and  
43 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-ḡalī* 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 17<sup>th</sup> century two additional sources of ashes were halophyte plants from Mediterranean countries (barilla) and algae harvested in northern Europe (kelp) (Ashtor and Cevdalli, 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 18<sup>th</sup> 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 19<sup>th</sup> 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 17<sup>th</sup> and 18<sup>th</sup> 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 Na<sub>2</sub>SO<sub>4</sub> with a series of consecutive reactions. The Leblanc process evolved into the Solvay process in the 19<sup>th</sup> 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).

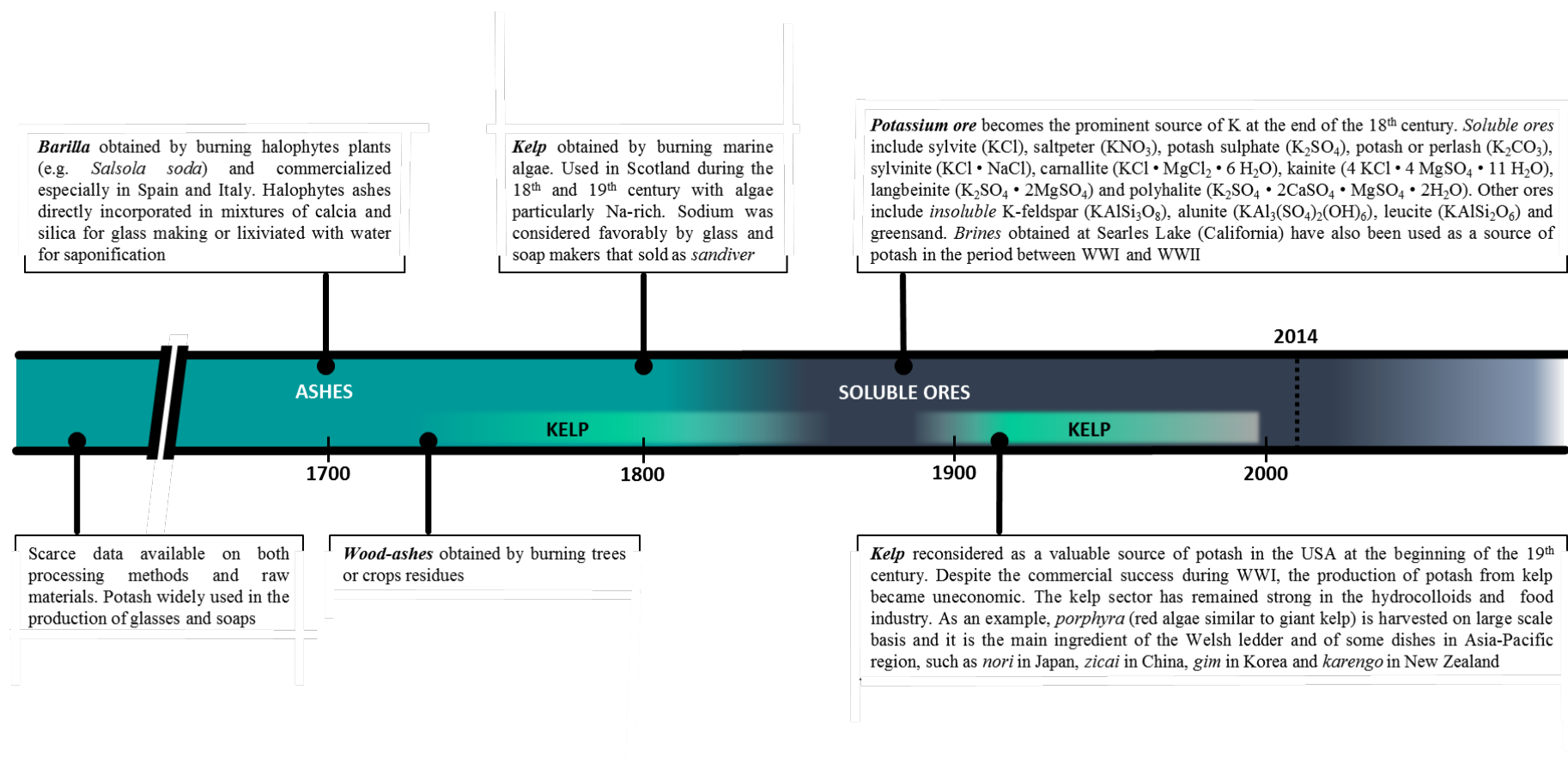


Figure 1 Timeline of the development of potash sources

## 2.2. The American wood ash industry

Before independence from England (16<sup>th</sup>-18<sup>th</sup> 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 18<sup>th</sup> 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 19<sup>th</sup> 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 frontier. 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,



1 indicating the beginning of the decline of the American potash industry from wood ashes. From the standpoint  
2 of the upcoming agricultural needs of the United States in the 19<sup>th</sup>-20<sup>th</sup> century, Browne used the expression  
3 *economic crime* to describe the decline of the early industry (Browne, 1926). He argues that when potash  
4 became appreciated for its fertilizing properties, its manufacturing had already disappeared in the USA and that  
5 almost two centuries of potash exports towards Europe impoverished American soils impeding agricultural  
6 development in the eastern United States (Browne, 1926).

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

### 20 **2.3. The German potash mining industry**

21  
22 Among the first references on the use of minerals as plant nutrients is the work of J. R. Glauber (16<sup>th</sup> century)  
23 (Darst, 1991). However, it was not until the 18<sup>th</sup> century that geological sources were adopted as fertilizers.  
24 Building on the early work of Karl Sprengel (1787-1859), Justus von Liebig (1803-1873) established that inorganic  
25 compounds and mineral sources could be used as a source of nutrients vital to plants and crops (Brock, 2002;  
26 Darst, 1991; De'sigmond, 1935; Lodge, 1938; Russel and Williams, 1977; Smil, 2004; Ulrich and Frossard, 2014;  
27 van der Ploeg et al., 1999). Their work was further complemented by the research of John B. Lawes (1814-1900)  
28 (Leonardos et al., 1987; Lodge, 1938; Russel and Williams, 1977; Ulrich and Frossard, 2014). With this new  
29 understanding, the old method of ash lixiviation was abandoned and the idea of mining potassium minerals  
30 became prominent. Potash mining had the clear advantage of being implementable on very large industrial  
31 scales, a concept acclaimed by the tycoons of the industrial revolution. Furthermore, the high K<sub>2</sub>O content in the  
32 final product allowed a significant reduction in transportation cost. Germany had extensive potash deposits  
33 formed during the Upper Permian, from the Zechstein Sea which was present in an area that now corresponds  
34 to a wide area of Central Europe (UK-Poland). Given a tradition of collaboration between government, academia  
35 and industry, Germany was an ideal location to test out the use of potassium minerals as fertilizers. Indeed,  
36 some of the driving forces behind the establishment of the potash industry can be attributed to the  
37 interventions exerted by the Prussian government as well as in the work of German scientists who were  
38 interested in the cultivation of potassium-demanding crops such as sugar beets (for the production of sucrose)  
39 or potatoes (as a staple food). The Permian Zechstein deposits were properly explored by 1843 and about 20  
40 years later, in 1861 they became commercially available in Stassfurt, mainly due to the work of Adolph Frank

(1834-1916) (Frank, 1893; Noyes, 1966; Russell and Williams, 1977; Tosdal, 1913). It was the turning-point in the history of potash. Almost



Photo from Illinois Agricultural Experiment Station

FIELD SHOWING THE VALUE OF POTASH TO THE FARMER

The soil is mucky and deficient in potash; the plot on the left has been enriched with potash, and yields a luxuriant crop. The center plot had no potash application, and the crop is scanty

**Figure 2** The importance of potash fertilizers as depicted by a photograph appeared in print in 1911 (Source: Mitchell GE. American potash for America. The National Geographic Magazine. XXII. National Geographic Society, Washington, 1911, pp. 399-405).

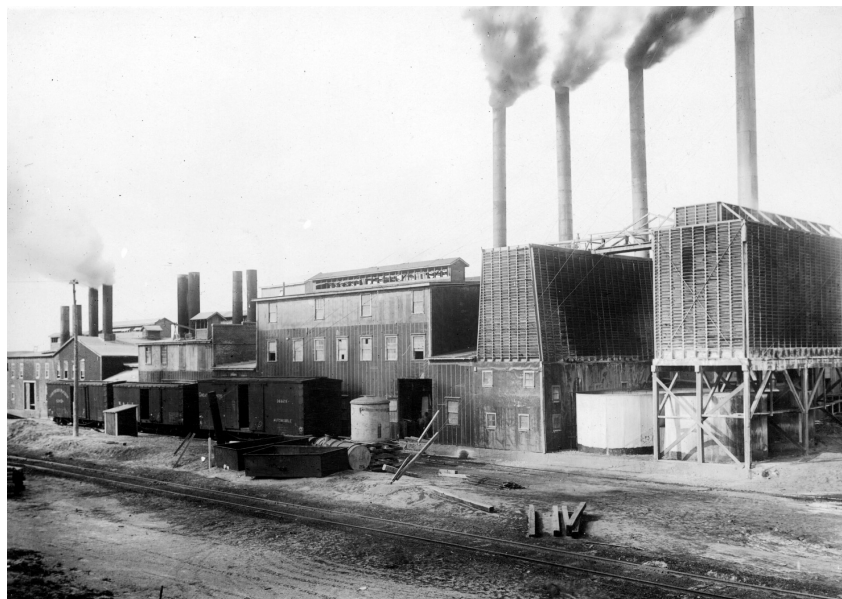
immediately, the ash market for glass and soap production was transformed into a global mining enterprise that targeted the agricultural sector. With a virtually complete monopoly, Germany became the world center of potash trade and remained so for about a century. In the USA, with the completion of 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 20<sup>th</sup> 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 20<sup>th</sup> 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  $K_2O$  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

1 important distribution center of wood ashes during the 19<sup>th</sup> century. However, like Russia, it properly  
2 developed its potash industry decades later (Anderson, 1985; Hart, 1912; Kreps, 1931; Miller, 1980).  
3



4  
5 **Figure 3 Photograph of The American Potash Company's plant operating in Antioch, Nebraska since 1916. Reprinted with permission**  
6 **from R.E. Jensen, *Nebraska's World War I Potash Industry*. Nebraska History, 1987. 68 pp. 28-42.**  
7

8 For the USA the hope of eroding part of the Franco-German cartel was little, unless local potash sources could  
9 be found as leverage. Two main solutions were proposed: exploration for local deposits and investigation of  
10 alternative potash sources (Dolbear, 1915; Hart, 1915; Howe, 1913; Meade, 1917; Stockett, 1918; Teeple, 1921;  
11 Turrentine and Shoaff, 1919). Mineral exploration began in 1911 (Anonymous, 1911b; Stockett, 1918;  
12 Turrentine, 1942). The following potash deposits were discovered: Sandhills, Nebraska (1912) (Jensen, 1987);  
13 Permian basin of Texas (1912; core not drilled until 1926) (Mansfield, 1923; Turrentine, 1938); Searles Lake,  
14 California (1913; operating since 1870s as a borax producer) (Mumford, 1938); Carlsbad, New Mexico (1926;  
15 commercial in 1931) (Cramer, 1938; Garrett, 1996; Jacob, 1958; Turrentine, 1942; Turrentine, 1943). The history  
16 of mineral exploration is well documented (Cramer, 1938; Garrett, 1996; Jensen, 1987; Mansfield, 1923;  
17 Mumford, 1938; Noyes, 1966; Turrentine, 1938; Turrentine, 1942; Turrentine, 1943). A second chapter of  
18 interest for the present world situation is that related to the sources of potash considered and investigated by  
19 American scientists. Here, we focus on four specific cases: i) the brine industry of Nebraska ii) the kelp industry  
20 of California, iii) production of potash from silicate minerals, and iv) production of potash from non-conventional  
21 sources (e.g. distillery residues or cement-kiln flue dusts).  
22

### 23 **3.1. The Nebraskan brine industry**

24

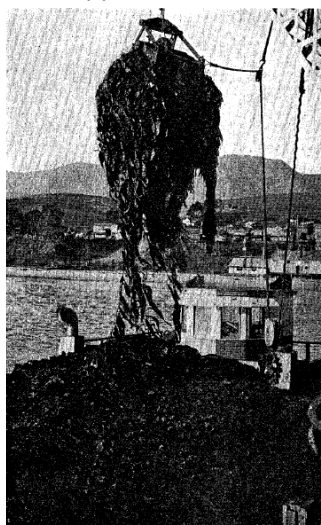
25 The short-lived production from brine in Nebraska is the very first attempt to establish an independent potash  
26 sector in the USA. Alkaline crusts from the western Sandhills area were known as early as 1900 (Gosselin et al.,  
27 1994; Hicks, 1921; Jensen, 1987). Brines were known and exploited elsewhere in the USA, including Salduro,  
28 Utah and, most notably, in Searles Lake, California (Hayes, 1942; Teeple, 1921). The Nebraskan industry started  
29 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  $K_2O$ /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  $K_2O$ /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  $K_2O$  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.

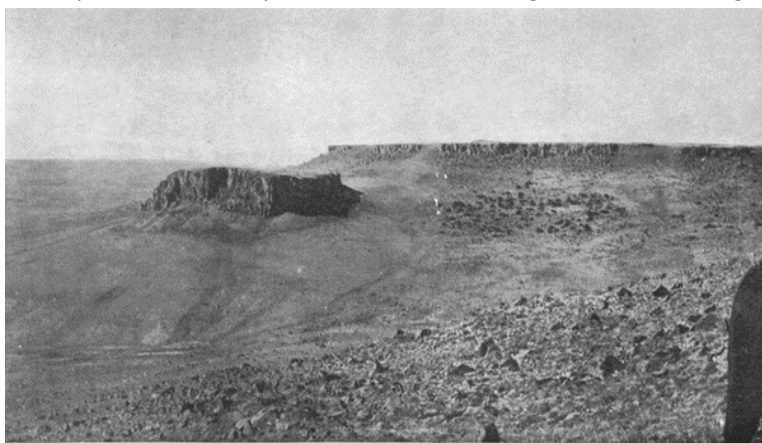
### 3.2. The Californian kelp industry

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 *Hercule 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.



(a)



NORTH TABLE MOUNTAIN, LEUCITE HILLS, WYOMING

This flat-topped mesa is capped by 50 to 100 feet of 8 to 11 per cent potash-bearing rock. The leucite area covers at least 10 square miles, and thus contains billions of tons of potash. Our granite hills also contain large percentages of potash, all at present unavailable, as no cheap method of extracting the potash has yet been developed.

(b)

Figure 4 (a) Kelp unloaded from a commercial harvester presumably in 1919 (Source: Turrentine JW, Shoaff PS. Potash from Kelp: the experimental plant of the United States Department of Agriculture. Preliminary Paper. Industrial & Engineering Chemistry 1919; 11: 864-874) (b) The leucite-rich hills of Wyoming as photographed in 1911 (Source: Mitchell GE. American potash for America. The National Geographic Magazine. XXII. National Geographic Society, Washington, 1911, pp. 399-405).

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 18<sup>th</sup> and 19<sup>th</sup> 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 20<sup>th</sup> 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 1 Overview of patented treatments proposed for the production of potash from K-feldspar (KFS).**

METHOD	PROCESS	REFERENCE
Wet chemistry	KFS+HF+CaSO <sub>4</sub> +T	(Doremus, 1913)
	KFS+H <sub>2</sub> SiF <sub>6</sub> +H <sub>2</sub> SO <sub>4</sub>	(Gibbs, 1904)
	KFS+H <sub>3</sub> PO <sub>4</sub>	(Robertson, 1919)
	KFS+Na(K)OH+T	(Frazer et al., 1916)
	KFS+(Na)K <sub>2</sub> CO <sub>3</sub> (or (Na)KOH)+T+P (see original)	(Frederick C. Gillen, 1917)
	KFS+CaCO <sub>3</sub> +T+P	(Andrews, 1919)
	KFS+CaF <sub>2</sub> +H <sub>2</sub> SO <sub>4</sub> +T	(Foote and Scholes, 1912)
	KFS+borax+(Na)K <sub>2</sub> CO <sub>3</sub> (or (Na)KOH)+T+P	(William H. Gillen, 1917)
Dry chemistry	KFS+HF (electrolysis)	(Cushman, 1907)
	KFS+NaCl	(Bassett, 1913a)
	KFS+NaCl+Na <sub>2</sub> CO <sub>3</sub>	(Bassett, 1914b)
	KFS+NaCl+CaCO <sub>3</sub>	(Rhodin, 1900a; Rhodin, 1900b)
	KFS+NaCl(or CaCl <sub>2</sub> )+CaSO <sub>4</sub>	(Morse and Sargent, 1912)
	KFS+NaNO <sub>3</sub>	(Blumenberg, 1919)
	KFS+Na <sub>2</sub> SO <sub>4</sub> +Na <sub>2</sub> CO <sub>3</sub>	(Bassett, 1913b)
	KFS+(K)NaCl+(K)NaHSO <sub>4</sub>	(Thompson, 1911)
	KFS+(K)NaCl+(K)NaHSO <sub>4</sub> +C	(Bassett, 1914a)
	KFS+soda ash (vitrification)	(Vanderburgh, 1864)
	KFS+(K)Na <sub>2</sub> O (see original)	(Rody, 1919)
	KFS+(Na)K <sub>2</sub> SO <sub>4</sub> +C	(Hart, 1913)
	KFS+(Na)K <sub>2</sub> CO <sub>3</sub> +H <sub>2</sub> O <sub>(g)</sub> +P	(Samuel Peacock, 1912b)
	KFS+K <sub>2</sub> SO <sub>4</sub> (or KHSO <sub>4</sub> )+SO <sub>2</sub>	(Neil, 1912)
	KFS+CaO+vapour	(Pohl, 1910)
	KFS+Ca(OH) <sub>2</sub> +P	(Gibbs, 1909)
	KFS+CaO+phosphate rock	(Benjamin Peacock, 1912)
	KFS+CaSO <sub>4</sub> +C	(Swayze, 1905)
	KFS+(Na)K <sub>2</sub> CO <sub>3</sub> (or (Na)KOH) (see original)	(Frederick C. Gillen, 1917)
	KFS+CaCO <sub>3</sub>	(Samuel Peacock, 1912a)
	KFS+CaCO <sub>3</sub>	(Brenner and Scholes, 1920)
	KFS+CaCO <sub>3</sub> +acid sludge	(Blumenberg, 1918)
	KFS+CaCO <sub>3</sub> (cement making)	(Spencer, 1915)
	KFS+Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(Haff, 1912)
	KFS+CaCO <sub>3</sub> (or Ca(OH) <sub>2</sub> )+CaF <sub>2</sub> +Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(Klett, 1865)
	KFS+NaCl+Ca(OH) <sub>2</sub>	(Edwards, 1919)
	KFS+Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> +CaCO <sub>3</sub>	(Bicknell, 1856)
	KFS+CaF <sub>2</sub>	(Mckirahan, 1921)
	KFS+CaCl <sub>2</sub> (or NaCl)+Fe (or Fe <sub>2</sub> O <sub>3</sub> )	(Glaeser, 1921)
	KFS+CaCl <sub>2</sub> +MgCl <sub>2</sub>	(Dyson and Grimshaw, 1979)
	KFS+CaCl <sub>2</sub> +CaO	(Blackmore, 1894)
	KFS+CaCl <sub>2</sub> +CaO	(Cushman, 1911)
	KFS+CaCl <sub>2</sub> +CaCO <sub>3</sub> (or MgCO <sub>3</sub> )	(Brown, 1915)
	KFS+CaSO <sub>4</sub> (or BaSO <sub>4</sub> or SrSO <sub>4</sub> )+CaCO <sub>3</sub>	(Tilghman, 1847)
	KFS+BaSO <sub>4</sub> +C	(Hart, 1911)

KFS+T	(Carpenter, 1910)
KFS+T (then aqueous solution of KOH)	(Swayze, 1907)
KFS+cement mixture+SO <sub>2</sub> (or O <sub>2</sub> )	(Schmidt, 1916)
KFS+C+Cl <sub>2</sub>	(Vivian and Fink, 1931)
KFS+Ca(Mg)O (or Na(K) <sub>2</sub> CO <sub>3</sub> )+CO <sub>2</sub>	(Gelleri, 1913)

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 (glaucinite) 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 17<sup>th</sup> and 18<sup>th</sup> 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 K<sub>2</sub>O. 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).



1  
2  
3  
4  
5

#### INSET - FUTURE SOURCES OF POTASH?

Mining of potash minerals remains economically advantageous due to the known chemical processing required on the raw material, the well-established technology for mining operations and the high concentration of  $K^+$  readily dissolved and available for plant growth. However, one might still wonder if some aspects of the early industries could be re-appreciated within the context of the modern world and its sustainability. Several local sources could contribute to substantial global amounts, as already happened in the USA during the 1910s and 1920s (Kreps, 1931).

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  $10^5$  t/year of ashes obtained by wood residues and an additional  $10^5$  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

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 20<sup>th</sup> 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 sylvinite 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 21<sup>st</sup> 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 20<sup>th</sup> Century, and is expected to propel innovation for the Global South in the 21<sup>st</sup> 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 21<sup>st</sup> 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.

## 8. REFERENCES

- A.A.V.V. The biology of seaweed. Los Angeles: Blackwell Scientific Publications, 1981.
- Adhia JD. Potash industry - worldwide. Chemical Age of India 1980; 31: 719-728.
- Anderson DL. Market power and the Saskatchewan potash industry. Canadian Public Policy/Analyse de Politiques 1985; 11: 321-328.
- Anderson E, Freeman MSJ. Process for obtaining potassium chloride. 1920; US1354642.
- Andrews AB. Method of extracting potash and the like. 1919; US1296035.
- Anonymous. Environmental Aspects of Phosphate and Potash Mining. United Nations Environment Programme and International Fertilizer Industry Association Paris, 2001.
- Anonymous. The German potash situation. The chemical trade journal and chemical engineer 1911a; 48: 77-79.
- Anonymous. Investigations of potash deposits. The journal of industrial and engineering chemistry 1911b: 948.
- Ashcroft EA. A neglected chemical reaction and an available source of potash. Institution of Mining and Metallurgy Bulletin 1917; 159: 1-20.
- Ashcroft EA. Discussion on "A neglected chemical reaction and an available source of potash". Institution of Mining and Metallurgy Bulletin 1918; 160: 1-20.
- Ashtor E, Cevdalli G. Levantine alkali ashes and European industries. Journal of European Economic History 1983; 12: 487-489.
- Azapagic A. Developing a framework for sustainable development indicators for the mining and minerals industry. Journal of cleaner production 2004; 12: 639-662.
- Barth TFW. Theoretical petrology: John Wiley & Sons, Inc., 1962.
- Bassett HP. Process of obtaining potash salts from feldspar. 1913a; US1072686
- Bassett HP. Treatment of aluminum-bearing materials. 1913b; US1079589.
- Bassett HP. Process of obtaining potash from feldspar. 1914a; US1091034.
- Bassett HP. Treatment of aluminum-bearing materials. 1914b; US1095306.
- Bernstein L. Effects of salinity and sodicity on plant growth. Annual Review of Phytopathology 1975; 13: 295-312.
- Bicknell C. Process of treating feldspar for a manure. 1856; US16111.
- Bixler HJ, Porse H. A decade of change in the seaweed hydrocolloids industry. Journal of Applied Phycology 2011; 23: 321-335.
- Blackmore. Process of making alkali salts. 1894; US513001.
- Blumenberg HJ. Process of extracting soluble potassium salt from feldspar, &c. 1918; US1286513.
- Blumenberg HJ. Process of making potassium nitrate. 1919; US1297640
- Boney AD. Aspects of the biology of the seaweeds of economic importance. In: Russell SFS, editor. Advances in marine biology. 3. Academic Press Inc., New York, 1965, pp. 105-253.
- Brenner RF, Scholes SR. Process of extracting potassium from potash-bearing silicate minerals. 1920.
- Brock WH. Justus von Liebig: The chemical gatekeeper: Cambridge University Press, 2002.
- Brown BJ, Hanson ME, Liverman DM, Merideth Jr RW. Global sustainability: toward definition. Environmental management 1987; 11: 713-719.
- Brown HE. Process of obtaining alkali-metal compounds 1915.
- Browne C. Historical notes upon the domestic potash industry in early colonial and later times. Journal of Chemical Education 1926; 3: 749-756.
- Brundtland GH. Address by Mrs Gro Harlem Brundtland Chairman at the Closing Ceremony of the Eighth and Final Meeting of the World Commission on Environment and Development. In: development Wcoea, editor, Tokyo, Japan, 1987.

- Buck EC. Bibliography on the Extraction of Potash. From complex mineral silicates, such as feldspar, leucite and glauconite (greensand marl). Metallurgical and chemical engineering 1918; XVIII: 33-37.
- Cameron FK. Waste and conservation of potash and phosphoric acid. Industrial & Engineering Chemistry 1912; 4: 169-172.
- Cameron FK. Potash from kelp: US Government Printing Office, 1915.
- Carpenter FR. Potash of rendering potash compounds soluble. 1910; US959841
- Chapman VJ, Chapman DJ. Seaweeds and their uses. New York: Chapman and Hall, 1980.
- Charlton HW. Recovery of Potash from Greensand. Industrial and Engineering Chemistry 1918; 10: 6-8.
- Clow A, Clow NL. The natural and economic history of kelp. Annals of Science 1947; 5: 297-316.
- Cordell D, Drangert J-O, White S. The story of phosphorus: Global food security and food for thought. Global environmental change 2009; 19: 292-305.
- Costanza R, Patten BC. Defining and predicting sustainability. Ecological Economics 1995; 15: 193-196.
- Cramer TM. Production of potassium chloride in New Mexico. Industrial & Engineering Chemistry 1938; 30: 865-867.
- Cranner, HB. Om vegetationsforsok med glimmerminera- lerne biotit og sericit som kalikilde. Nor. geol. unders. Bull. 1922; 14; 37 pp.
- Crutzen PJ. Geology of mankind. Nature 2002; 415: 23-23.
- Crutzen PJ. The "anthropocene". Earth System Science in the Anthropocene. Springer, 2006, pp. 13-18.
- Cushman AS. Method of extracting potash from feldspathic or other potash-bearing rock. 1907; US851922
- Cushman AS. Method of treating rocks containing potassium. 1911; US987436
- Cushman AS, Coggeshall GW. The production of available potash from the natural silicites. Journal of the Franklin Institute 1912; 174: 663-678.
- Cushman AS, Hubbard P. The extraction of potash from feldspathic rock. Journal of the American Chemical Society 1908; 30: 779-797.
- Darst BC. Development of the potash fertilizer industry. Fertilizer research 1991; 28: 103-107.
- De'sigmond AAJ. Development of soil science. Soil Science 1935; 40: 77-88.
- Dolbear S. The potash situation. Metallurgical and chemical engineering 1915; 13: 481-482.
- Dold B. Sustainability in metal mining: from exploration, over processing to mine waste management. Reviews in Environmental Science and Bio/Technology 2008; 7: 275-285.
- Doremus CA. Process of making potassium sulphate. 1913.
- Dyson P, Grimshaw RW. Production of alkali metal chlorides. 1979; EP1979300122.3.
- Edwards RS. Process of extracting potassium salts. 1919.
- Ellis C. Process of obtaining cement and soluble potassium compounds. 1916; US1186522
- España-Gamboa E, Mijangos-Cortes J, Barahona-Perez L, Dominguez-Maldonado J, Hernández-Zarate G, Alzate-Gaviria L. Vinasses: characterization and treatments. Waste Management & Research 2011; 29: 1235-1250.
- FAOSTAT database, Food and Agriculture Organization of the United Nations. 2013.
- Foot HW, Scholes SR. The Extraction of potash and alumina from feldspar. Industrial & Engineering Chemistry 1912; 4: 377-377.
- Fortune S., Hollies J. and Stockdale E.A. Effects of different potassium fertilizers suitable for use in organic farming systems on grass/clover yields and nutrient offtakes and interactions with nitrogen supply. Soil Use and Management 2004; 20: 403-409.
- Frank A. Zur Geschichte der Kalidüngerfabrikation in Stassfurt. Zeitschrift für angewandte Chemift 1893; 6: 325-326.
- Frazer JCW, Holland WW, Miller E. Method of treating mineral silicates. 1916; US1196734

Frederick WH. Process of recovering water-soluble potassium salts from feldspathic rocks or their derivatives in the manufacture of Portland cement. 1916; US1194344

Freeman MSJ. Process for obtaining potassium chloride. 1922; US1402173

Frink CR, Waggoner PE, Ausubel JH. Nitrogen fertilizer: retrospect and prospect. Proceedings of the National Academy of Sciences 1999; 96: 1175-1180.

Gale HS. Potash. Mineral Resources. Department of the Interior - United States Geological Survey, Washington, 1919a, pp. 81-84.

Gale HS. Potash deposits in Spain. Engineering and Mining Journal 1919b; 108: 758-763.

Gale HS. The potash deposits of Alsace. Vol Bulletin 715. Washington: US Government Printing Office, 1920.

Gale W. Chemistry of the Trona Process from the Standpoint of the Phase Rule. Industrial & Engineering Chemistry 1938; 30: 867-871.

Garrett DE. Potash: deposits, processing, properties and uses: Chapman & Hall London, UK; 1996.

Gelleri S. Method of recovering alkalis from silicates. 1913; US1078496

Gibbs WT. Process of decomposing refractory silicates. 1904; US772612

Gibbs WT. Process of making caustic alkalis. 1909; US910662

Gillen FC. Process for obtaining potash from potash-rock. 1917; US1215517

Gillen WH. Process for decomposing feldspar and other potash-bearing silicious minerals. 1917; US1215518.

Gillispie CC. The discovery of the Leblanc process. ISIS 1957; 48: 152-170.

Glaeser W. Method of treating potash-bearing silicates. 1921; US1379914

Goldschmidt, VM. Oversiktskart over utbredelsen av de forskjellige kalimineraler i norsk fjeldgrund. Norsk Landmansblad. 1922; 41, 268-269.

Goldschmidt, VM. and Johnsen, E. Glimmermineralernes betydning som kalikilde for planterne. 1922: Nor. geol. unders. Bull. 108. 89pp.

Gosselin DC, Sibray S, Ayers J. Geochemistry of K-rich alkaline lakes, Western Sandhills, Nebraska, USA. Geochimica et Cosmochimica Acta 1994; 58: 1403-1418.

Haff MM. Process of obtaining alkali-metal compounds from minerals containing alkalis. 1912; US 1018186

Hager T. The alchemy of air: A Jewish genius, a doomed tycoon, and the scientific discovery that fed the world but fueled the rise of Hitler: Random House Digital, Inc., 2008.

Hart E. Process of extracting potash salts and other products from silicious rocks. 1911.

Hart E. Potash, silica and alumina from feldspar. Industrial & Engineering Chemistry 1912; 4: 827-828.

Hart E. Process of making potash alum. 1913; US1062278

Hart E. The potash situation. Industrial & Engineering Chemistry 1915; 7: 670-671.

Hayes SP. Potash prices and competition. The Quarterly Journal of Economics 1942; 57: 31-68.

Hicks WB. Potash resources of Nebraska. Contributions to Economic Geology - Part I. US Government Printing Office, Washington, 1921, pp. 125-139.

Hite RJ, Japakasetr T. Potash deposits of the Khorat plateau, Thailand and Laos. Economic Geology 1979; 74: 448-458.

Holmes A. I.- Non-german sources of potash. Geological magazine 1919; 6: 340-350.

Holwerda JG, Hutchinson RW. Potash-bearing evaporites in the Danakil area, Ethiopia. Economic Geology 1968; 63: 124-150.

Hornsey JW. Potash from desert lakes and alunite. Industrial & Engineering Chemistry 1918; 10: 838-839.

Howe MA. Fertilizer resources of the United States. Torreya 1913; 13: 220-223.

<http://remineralize.org/>. Accessed on 17th June 2014.

Huber FW, Reath FF. Process of producing cement and recovering potassium compounds. 1917; US1219315

Jackson DD. Process for the recovery of potash from cement mixtures. 1922; US1415572.

Jacob KD. Fifty years of fertilizer progress. *Industrial & Engineering Chemistry* 1958; 50: 40A-43A.

James AK, Thring RW, Helle S, Ghuman HS. Ash management review—applications of biomass bottom ash. *Energies* 2012; 5: 3856-3873.

Jasinski, S.M. 2011. Mineral Commodity Summaries (2011) Potash  
<http://minerals.usgs.gov/minerals/pubs/commodity/potash>

Jensen RE. Nebraska's World War I Potash Industry. *Nebraska History* 1987: 28-42.

Klett F. Improvement in the manufacture of fertilizers. 1865; US49891.

Kreps TJ. Vicissitudes of the American potash industry. *Journal of Economic and Business History* 1931; III: 630-666.

Kurrelmeyer LH. The Potash Industry. In: Mexico DorDogUoN, editor. Analysis of recent developments in the economics of the potash industry with particular reference to Carlsbad, New Mexico, Albuquerque, 1951, pp. 83.

Lam CH, Ip AW, Barford JP, McKay G. Use of incineration MSW ash: a review. *Sustainability* 2010; 2: 1943-1968.

Ladeira PLG. Potash product and method. 2013; PCT/GB2012/052687.

Lélé SM. Sustainable development: a critical review. *World development* 1991; 19: 607-621.

Leonardos OH., Fyfe WS, Kronberg BI. The use of ground rocks in laterite systems: an improvement to the use of conventional soluble fertilizers? *Chemical Geology* 1987; 60: 361-370.

Leonardos OH, Theodoro SH., Assad ML. Remineralization for sustainable agriculture: a tropical perspective from a Brazilian viewpoint. *Nutrient Cycling in Agroecosystems* 2000; 56: 3–9.

Lodge F. Potash in the Fertilizer Industry. *Industrial & Engineering Chemistry* 1938; 30: 878-882.

Lüttge U., Clarkson DT. Mineral nutrition: potassium. *Progress in botany*. 50. Springer, 1989, pp. 51-73.

MacDonald GK, Bennett EM, Potter PA, Ramankutty N. Agronomic phosphorus imbalances across the world's croplands. *Proceedings of the National Academy of Sciences* 2011; 108: 3086-3091.

Manning DAC. Mineral sources of potassium for plant nutrition. A review. *Agronomy for Sustainable Development* 2010; 30: 281-294.

Manning DAC. Plant nutrients. In: Hester RE, Harrison RM, editors. *Soils and food security*. Royal Chemical Society, Cambridge, UK, 2012.

Mansfield GR. The Potash Field in Western Texas. *Industrial & Engineering Chemistry* 1923; 15: 494-497.

Mason M. Victor Moritz Goldschmidt: Father of Modern Geochemistry. *Geochemical Society, Special Publication* 1992; 4; 184pp.

Maxey DW. Inventing History: the holder of the first US patent. *Journal of the Patent and Trademark Office Society* 1998a; 80: 155-170.

Maxey DW. Samuel Hopkins, the Holder of the first US patent: a study of failure. *The Pennsylvania Magazine of History and Biography* 1998b; 122: 3-37.

Mckirahan S. Extraction of potassium from the natural substances in which it occurs. 1921; US1388276.

Meade R, K. The possibilities of developing an american potash industry. *Metallurgical and chemical engineering* 1917; XXVII: 78-87.

Merz AR, Lindemuth JR. The Leaching of potash from freshly cut kelp. *Industrial & Engineering Chemistry* 1913; 5: 729-730.

Merz AR, Ross WH. The Nature of the recombined potash in cement mill dust. *Industrial & Engineering Chemistry* 1919; 11: 39-45.

Miller H. Potash from wood ashes: frontier technology in Canada and the United States. *Technology and culture* 1980; 21: 187-208.

Mohme FS. The potash industry of Europe. *Economic Geography* 1929; 5: 141-148.



Morse HW, Sargent LW. Process of treating feldspar. 1912; US1041327

Mueller ND, Gerber JS, Johnston M, Ray DK, Ramankutty N, Foley JA. Closing yield gaps through nutrient and water management. *Nature* 2012; 490: 254-257.

Mumford R. Potassium Chloride from the Brine of Searles Lake. *Industrial & Engineering Chemistry* 1938; 30: 872-878.

Neil JM. Process of obtaining potash from feldspar. 1912; US1034281

Neushul P. Seaweed for war: California's World War I kelp industry. *Technology and culture* 1989; 30: 561-583.

Noyes R. Potash and Potassium Fertilizers. In: Corporation ND, editor. Chemical process monograph 1966.

Obersteiner M, Peñuelas J, Ciais P, van der Velde M, Janssens IA. The phosphorus trilemma. *Nature geoscience* 2013; 6: 897-898.

Öborn I, Andrist-Rangel Y, Askegaard M, Grant C, Watson C, Edwards A. Critical aspects of potassium management in agricultural systems. *Soil Use and Management* 2005; 21: 102-112.

Östlund L, Zackrisson O, Strotz H. Potash production in northern Sweden: history and ecological effects of a pre-industrial forest exploitation. *Environment and History* 1998; 4: 345-358.

Peacock B. Process of producing potassium hydrogen phosphate. 1912; US1046327

Peacock S. Process for extracting alumina and potash from feldspar. 1912a; US1035812

Peacock S. Process for the recovery of silica, alumina and potash from feldspar. 1912b; US1030122

Piazzese S. Twenty-five years of the Italian potash industry. *Phosphorus and potassium* 1987: 46-47.

Pohl E. Process of preparing mineral fertilizers. 1910; US952278

Rao JR, Nayak R, Suryanarayana A. Feldspar for potassium, fertilisers, catalysts and cement. *Asian Journal of Chemistry* 1998; 10: 690-706.

Retvedt, K. Kalivirkningen av glimmer, feltspat og leir. *Meld. Norg. Landbr. Hogskole* 1938; 18; 127-182.

Rhodin JGA. A process for the production of soluble potassium salts from feldspar (orthoclase). 1900a; GB16780.

Rhodin JGA. Process of obtaining soluble potassium salts from felspar. 1900b; US641406.

Rhodin JGA. Production of soluble potash salts from potassium felspar (orthoclase). *The journal of the society of chemical industry* 1901; XX: 439-440.

Richert A, Gensch R, Jönsson H, Stenström TA, Dagerskog L. Practical guidance on the Use of Urine in Crop Production. *EcoSanRes Programme*, Stockholm Environment Institute, Stockholm, Sweden, 2010.

Rittenhouse P. Potash and politics. *Economic Geology* 1979; 74: 353-357.

Roberts WII. American potash manufacture before the American revolution. *Proceedings of the American philosophical society* 1972; 116: 383-395.

Robertson FDS. Process of extracting potassium from its insoluble compounds. 1919; 1317524.

Rody FA. Treatment of feldspar, leucite and the like. 1919; US1325882.

Römheld V, Kirkby EA. Research on potassium in agriculture: needs and prospects. *Plant and Soil* 2010; 335: 155-180.

Ross WH. The Decomposition of Feldspar and Its Use in the Fixation of Atmospheric Nitrogen. *Industrial & Engineering Chemistry* 1913; 5: 725-729.

Ross WH. The extraction of potash from silicate rocks—II. *Industrial & Engineering Chemistry* 1917; 9: 467-472.

Ross WH, Merz AR. The Recovery of potash as a by-product in the blast furnace industry. *Industrial & Engineering Chemistry* 1922; 14: 302-303.

Ross WH, Merz AR, Wagner CR. The recovery of potash as a by product in the cement industry. *United States Department of Agriculture, Washington, D.C., 1917*, pp. 1-23.

Rozema J, Flowers T. Crops for a salinized world. *Science* 2008; 322: 1478-1480.

Russel DA, Williams GG. History of chemical fertilizer development. *Soil Science Society of America Journal* 1977; 41: 260-265.

Saurat A. Potash fertilization in Arab countries. Research results. International Potash Institute, Bern, Switzerland, 1989, pp. 1-10.

Sheehan G, Greenfield P. Utilisation, treatment and disposal of distillery wastewater. *Water Research* 1980; 14: 257-277.

Scherer HW, Mengel K, Dittmar H, Drach M, Vosskamp R, Trenkel ME, et al. Fertilizers. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, 2002.

Schmidt WA. Process of obtaining alkali-metal compound from silicates. 1916; US1200887.

Scholz RW, Wellmer FW (2013). Approaching a dynamic view on the availability of mineral resources: what we may learn from the case of phosphorus?. *Global Environmental Change* 2013, 23: 11-27.

Sheldrick, WF., Lingard J. The use of nutrient audits to determine nutrient balances in Africa. *Food Policy* 2004; 29: 61-98.

Sheldrick, WF., Syers, JK., Lingard, J. A conceptual model for conducting nutrient audits at national, regional and global scales. *Nutrient Cycling in Agroecosystems* 2002; 62; 61-67.

Shreve RN. Potash. *Journal of Chemical Education* 1927; 4: 230-241.

Smil V. *Enriching the earth: Fritz Haber, Carl Bosch, and the transformation of world food production*: The MIT press, 2004.

Smith HI. Developments affecting the American potash industry. *Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers* 1936; 129: 343-352.

Smith LJ. On the determination of the alkalies in silicates by ignition with carbonate of lime and salamoniac. *American Journal of Science* 1871; 2: 269-275.

Solberg P. Forsok moo glimmer, feldspat og leir som kali-holdig jordtorbedringsmiddel. *Med. Norg. Landbr. Hogskole* 1928; 8; 419-482 .

Somerwill K, Hugo S, Crowe A, Boatman N, Hart A, Laybourn R, et al. Future Need and Role of Potash in UK Food Production. In: agency TfaEr, editor, 2012.

Spackman HS, Conwell EL. Process of recovering alkali. 1916; US1202327.

Spencer AC. Process of recovering potash. 1915.

Spencer G. Potash from Kelp. III-The Preliminary Examination of Kelp Distillates. *Industrial & Engineering Chemistry* 1920; 12: 786-792.

Spencer GC. Potash From Kelp. II-The Experimental Distillation of Kelp at Low Temperatures. *The journal of industrial and engineering chemistry* 1920; 12: 682-684.

Spiller J. Feldspar as a source of potash alum. *Journal of the Franklin Institute* 1882; 114: 122-124.

Stockett AW. The potash situation. *Industrial & Engineering Chemistry* 1918; 10: 918-920.

Swayze AJ. Process of making potassium salts. 1905; US789074.

Swayze AJ. Extraction of potassium compounds from feldspar. 1907; US862676.

Tanner H. Potash from Kelp. VI-The Decolorizing Action of Adsorptive Charcoals. *Industrial & Engineering Chemistry* 1922; 14: 441-443.

Teeple JE. The American potash industry and its problems. *The journal of industrial engineering chemistry* 1921; 13: 249-252.

The New York Times Editorial Board. Collusion in the Potash Market. *The New York Times*, September 13, 2013 p. A18.

Thieme C. Sodium Carbonates. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, 2002.

Thompson F. Process of obtaining potash salts from feldspar. 1911.

Tilghman RA. Improvement in decomposing potash feldspar for obtaining certain salts. 1847; US5384.

- Tilman D, Cassman KG, Matson PA, Naylor R, Polasky S. Agricultural sustainability and intensive production practices. *Nature* 2002; 418: 671-677.
- Tite M, Shortland A, Maniatis Y, Kavoussanaki D, Harris S. The composition of the soda-rich and mixed alkali plant ashes used in the production of glass. *Journal of Archaeological Science* 2006; 33: 1284-1292.
- Tosdal HR. The Kartell Movement in the German Potash Industry. *The Quarterly Journal of Economics* 1913; 28: 140-190.
- Turrentine J, Tanner H. Potash from Kelp. V-The Applicability of Kelpchar as a Bleaching and Purifying Agent. *Industrial & Engineering Chemistry* 1922; 14: 19-24.
- Turrentine J, Tanner H, Shoaff P. Potash from Kelp. VII-The Manufacture of Potash Salts. *Industrial & Engineering Chemistry* 1923; 15: 159-163.
- Turrentine JW. American potash—A progress report. *Industrial & Engineering Chemistry* 1924; 16: 1192-1193.
- Turrentine JW. The potash situation in 1931. *Commercial fertilizer year book*, 1932, pp. 27-30.
- Turrentine JW. Symposium on potash. *Industrial & Engineering Chemistry* 1938; 30: 853-853.
- Turrentine JW. Wartime Contribution of the American Potash Industry. *Industrial and Engineering Chemistry* 1942; 34: 1422-1426.
- Turrentine JW. Potash in North America. New York: Reinhold Publishing Corporation, 1943.
- Turrentine JW. The American potash industry meets its wartime test. *Chemical & Engineering news* 1944; 22: 1994-1998.
- Turrentine JW, Shoaff PS. Potash from Kelp: the experimental plant of the United States Department of Agriculture. Preliminary Paper. *Industrial & Engineering Chemistry* 1919; 11: 864-874.
- Turrentine JW, Shoaff PS. Potash from Kelp. IV-Continuous Countercurrent Lixiviation of Charred Kelp. *Industrial & Engineering Chemistry* 1921; 13: 605-609.
- Ulrich AE, Frossard E. On the history of a reoccurring concept: Phosphorus scarcity. *Science of The Total Environment* 2014; 490: 694-707.
- van der Ploeg RR, Böhm W, Kirkham MB. On the origin of the theory of mineral nutrition of plants and the law of the minimum. *Soil Science Society of America Journal* 1999; 63: 1055-1062.
- Van Straaten P. Rocks for crops: Agrominerals of sub-Saharan Africa. ICRAF, Nairobi, Kenya, 2002.
- Van Straaten P. Farming with rocks and minerals: challenges and opportunities. *Anais da Academia Brasileira de Ciências* 2006; 78: 731-747.
- Vanderburgh GE. Improvement in treating feldspar to obtain useful products. 1864; US43534.
- Vinogradov AP. The elementary chemical composition of marine organisms. Vol Number II. New Heaven, 1953.
- Vivian RE, Fink CG. Combined process of extracting the phosphorus content from phosphorus containing materials and the potassium content from potassium containing materials. 1931; US1926073.
- Wilkie AC, Riedesel KJ, Owens JM. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. *Biomass and Bioenergy* 2000; 19: 63-102.
- Woods, PJE. The geology of Boulby Mine. *Economic Geology*, 1979; 74: 409-418.
- Yasuda M, Warwick KDPCG. A molten phosphorus-potassium fertilizer, and its preparation process. 2013; WO2013063667 A1.
- Yuan J, Zhao Y, Li Q, Ji Z, Guo X. Preparation of potassium ionic sieve membrane and its application on extracting potash from seawater. *Separation and Purification Technology* 2012; 99: 55-60.
- Zhang F-S, Yamasaki S, Kimura K. Waste ashes for use in agricultural production: II. Contents of minor and trace metals. *Science of the total environment* 2002a; 286: 111-118.
- Zhang F-S, Yamasaki S, Nanzyo M. Waste ashes for use in agricultural production: I. Liming effect, contents of plant nutrients and chemical characteristics of some metals. *Science of the total Environment* 2002b; 284: 215-225.

Zhang P-J, Zhao Z-G, Yu S-J, Guan Y-G, Li D, He X. Using strong acid–cation exchange resin to reduce potassium level in molasses vinasses. *Desalination* 2012; 286: 210-216.

## SUPPLEMENTARY MATERIAL

### Historical and technical developments of potassium resources

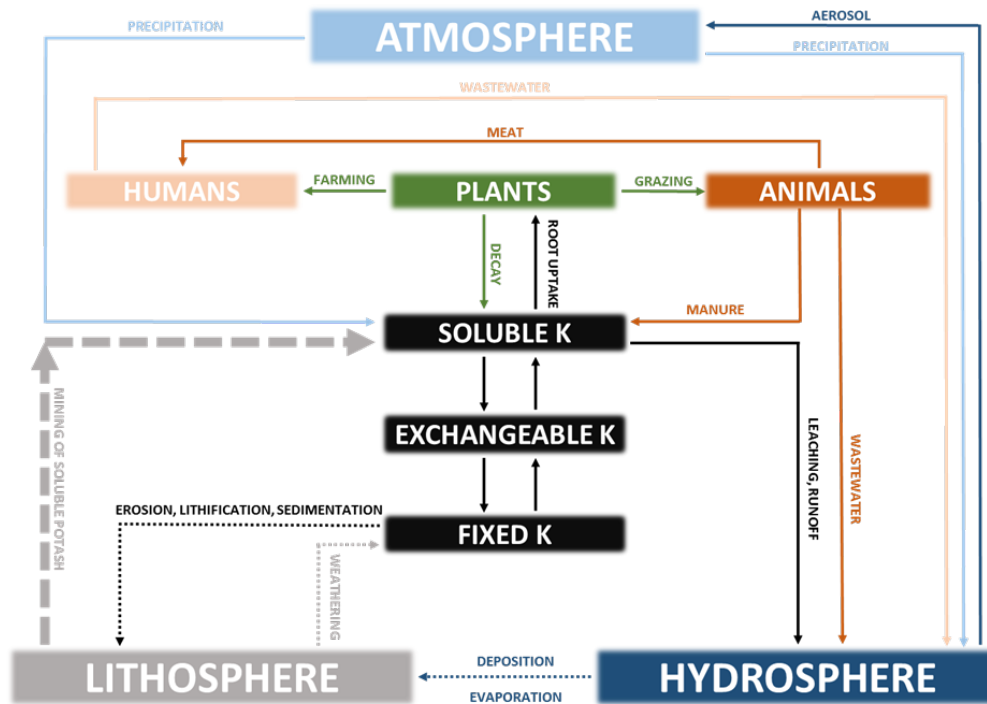
**Davide Ciceri<sup>a</sup>, David A.C. Manning<sup>b</sup> and Antoine Allanore<sup>a</sup>**

<sup>a</sup> Department of Materials Science & Engineering. Room 13-5066 Massachusetts Institute of Technology. 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA. Email: ciceri@mit.edu

<sup>b</sup> School of Civil Engineering and Geosciences Room 3.01 Drummond Building. Newcastle University. Newcastle upon Tyne NE1 7RU, UK. Email: david.manning@ncl.ac.uk

**Corresponding author:** Antoine Allanore, Department of Materials Science & Engineering. Room 13-5066 Massachusetts Institute of Technology. 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA. Email: allanore@mit.edu

## 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 ( $\text{KAlSi}_3\text{O}_8$ ) and micas (e.g.  $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ) (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).  $\text{K}^+$  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  $1.1 \times 10^{-3} \text{ t} \cdot \text{person}^{-1} \cdot \text{yr}^{-1}$  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  $10^7 \text{ t/year}$  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  $\approx 0.6$  wt %) can be found in marine organisms such as *kelp*. This observation correlates well with the long residence time of  $K^+$  in the ocean ( $\approx 10^7$  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  $10^{-7} \text{ t} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  (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 (3<sup>rd</sup> millennium BC) (Tite et al., 2002). The Bible mentions the use of *lye* in the book of Jeremiah (7<sup>th</sup>-6<sup>th</sup> centuries BC) (Jeremiah). Glass-making with potash is described by Pliny the Elder (1<sup>st</sup> 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 18<sup>th</sup> 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 30<sup>th</sup> 1914, the USA imported 1,066,929 t of potash to be used as fertilizers. During the subsequent six months, July 1<sup>st</sup> - December 31<sup>st</sup> 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)



## REFERENCES

- Anonymous. The German potash situation. The chemical trade journal and chemical engineer 1911a; 48: 77-79.
- Barth TFW. Theoretical petrology: John Wiley & Sons, Inc., 1962.
- Bradshaws W, Henry. The production of potash from feldspar. PhD Thesis. Chemical engineering. Massachusetts Institute of Technology, 1907.
- Burkhardt ER. Potassium and potassium alloys. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, 2002.
- Cushman AS. Chemistry and american industry. Journal of the Franklin Institute 1917; 183: 557-574.
- de Turk E. Potassium-bearing minerals as a source of potassium for plant growth. PhD Thesis. University of Illinois, 1919.
- Davy H. The Bakerian lecture: On some new phenomena of chemical changes produced by electricity, particularly the decomposition of the fixed alkalies, and the exhibition of the new substances which constitute their bases; and on the general nature of alkaline bodies. Philosophical Transactions of the Royal Society of London 1808; 98: 1-44.
- Dolbear S. The potash situation. Metallurgical and chemical engineering 1915; 13: 481-482.
- Gallup HW. The recovery of potash salts from feldspar. Chemistry. PhD Thesis. Massachusetts Institute of Technology, 1905.
- Hardie LA. Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y. Geology 1996; 24: 279-283.
- Haynes WM, Lide DR, Bruno TJ. CRC Handbook of Chemistry and Physics 2012-2013: CRC press, 2012.
- Herrington R. Road map to mineral supply. Nature geoscience 2013; 6: 892-894.
- Jensen RE. Nebraska's World War I Potash Industry. Nebraska History 1987: 28-42.
- Jeremiah. The New American Bible, Revised Edition (NABRE). USCCB.
- Kreps TJ. Vicissitudes of the American potash industry. Journal of Economic and Business History 1931; III: 630-666.
- Iyengar GV, Kollmer WE, Bowen HJM. The elemental composition of human tissues and body fluids: a compilation of values for adults, 1978.
- Manning DAC. Mineral sources of potassium for plant nutrition. A review. Agronomy for Sustainable Development 2010; 30: 281-294.
- Mitchell GE. American potash for America. The National Geographic Magazine. XXII. National Geographic Society, Washington, 1911, pp. 399-405.
- Meade R, K. The possibilities of developing an american potash industry. Metallurgical and chemical engineering 1917; XXVII: 78-87.
- Richert A, Gensch R, Jönsson H, Stenström TA, Dagerskog L. Practical guidance on the Use of Urine in Crop Production. EcoSanRes Programme, Stockholm Environment Institute, Stockholm, Sweden, 2010.
- Shreve RN. Potash. Journal of Chemical Education 1927; 4: 230-241.
- Spaargaren D, Ceccaldi H. Some relations between the elementary chemical-composition of marine organisms and that of sea-water. Oceanologica acta 1984; 7: 63-76.
- Stockett AW. The potash situation. Industrial & Engineering Chemistry 1918; 10: 918-920.
- Tite M, Shortland A, Paynter S. The beginnings of vitreous materials in the Near East and Egypt. Accounts of chemical research 2002; 35: 585-593.
- Turrentine JW. Wartime Contribution of the American Potash Industry. Industrial and Engineering Chemistry 1942; 34: 1422-1426.
- Williams KR. Fertilizers, then and now. Journal of Chemical Education 2010; 87: 135-138.
- Yanyi G. Raw materials for making porcelain and the characteristics of porcelain wares in north and south China in ancient times. Archaeometry 1987; 29: 3-19.