

EDUCATOR

THE RISE AND FALL OF THE SALITRE (SODIUM NITRATE) INDUSTRY

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Abstract

The nitrate fields in Chile are exceptional for their mineral content and unknown origin and serve as an excellent example how a chemical technology can arise to create a very large and almost exclusive market, to be sent then almost into oblivion by competing technologies. The income from sodium nitrate export provided for many years almost 50% of the income of the Chilean government and a large part of the world needs for fertilizers. Development of the Haber-Bosch process for ammonia synthesis resulted in the crash of the dream and a serious economic crisis for Chile.

The rise and fall of the salitre industry in Chile is a fascinating example of human effort, greed, commercial and political plots, a bloody five-year long war among three countries, and the never ending saga of one technology brutally replacing another. In this work we present the general background of the subject, a description of the geology and theories on the origin of the nitrate fields, as well as historical facts of the development of the extraction technologies up to beginning of commercial ammonia production by the Haber-Bosch process.

Introduction

Only very few soils on earth are so well provided with nutrients that they can provide high crop yields over prolonged periods without any fertilization. In the most favorable cases, fertilization is done by natural processes, as the one occurring with the Nile river. Ordinarily the opposite situation is true, namely there is more or less rapid impoverishment of the soil through the growing of crops. In the past, the demand for major nutrients was met by application of animal and human wastes to the land and in modern times with chemical fertilizers. Continuous yield of foodstuffs from any area of land must inevitably decrease if

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the land is continuously cultivated and these nutrients are not replaced. Fertilization serves to obtain high crop yields and good quality produce.

Agriculture has been concerned with fertilizers since antiquity and the history of fertilization is an essential part of the history of agriculture. Experience with fertilization in early times was described many times in the classical literature, for example, Homer mentions manure as a fertilizer in the *Odyssey*. Certain fertilizers were considered so valuable in antiquity, that their theft was considered a punishable offense. *Stercutius* in ancient Rome was made immortal by the gods for his invention of fertilization. Among the different materials used in antiquity to supplement soil fertility, we can mention farmyard manure and compost, vegetable and animal waste (straw, blood, etc.), human and animal excrement, bird excrement deposits (guano), seaweed, salt-containing earths, ash, etc.¹ [Fick, A. *Fertilizers and Fertilization*. Verlag Chemie: Weinheim, 1982.].

Fertilizers may be described as mixtures that are applied to agricultural land to restore nutrients removed from the soil by crop plants. The major nutrient elements removed by crops are potassium, phosphorus, and nitrogen and the fertilizers must supply these in soluble form.

In the beginning fertilizers were called *dung*, from the old German word *tung*, meaning a storage pit covered with manure for protection against the cold. From this was derived the word dung (fertilizer) as the cover. The corresponding English term *fertilizer*, was derived from the Latin root *fertil* (fertile).

Nitrogen constitutes about 79% of the earth's atmosphere. It is used almost entirely in chemical combination with other elements and its most important role is a primary crop nutrient. Fixed nitrogen is supplied in rainwater and atmospheric nitrogen is fixed by certain leguminous crops that are included in the crop rotational system. Nitrogen is one of the three primary plant nutrients. About 85% of nitrogen is used to produce nitrogen fertilizers and the remainder goes into a wide range of industrial products such as synthetic fibers, explosives, animal feed-stuffs, etc. Almost all nitrogen products are manufactured from ammonia, which is derived from the catalytic fixation of nitrogen from the atmosphere with hydrogen, obtained from a variety of hydrocarbons, but mainly natural gas.

All living matter contains considerable amounts of chemically combined nitrogen, which is essential for the growth of living organisms. Animals cannot assimilate free nitrogen from the air and depend upon plants for their supply. No plant or animal can use atmospheric nitrogen directly but prokaryotes, such as bacteria and blue-green algae, are able to do so. Nitrogen fixation is done by non-symbiotic bacteria such as cyanobacteria (or blue-green algae) and symbiotic bacteria such as *Rhizobium*, associated with leguminous plants, and *Spirillum lipoferum*, associated with cereal grasses. In the blue-green algae,

photosynthesis and fixation of atmospheric nitrogen occur in the same organism, while in bacteria this does not happen. Rhizobia bacteria synthesize ammonia from atmospheric nitrogen and carbohydrates provided by the plant, which in turn uses this fixed nitrogen. The symbiotic nitrogen-fixing bacteria invade the root hairs of host plants, where they multiply and stimulate the formation of root nodules, enlargements of plant cells and bacteria in intimate association. Within the nodules the bacteria convert free nitrogen to nitrates, which the host plant uses for its development.

Plants that cannot assimilate free nitrogen get it from the soil in the form of nitrates, ammonium salts, or other nitrogen compounds arising from the decay of living matter. Nitrogen is fixed, or combined, in nature as nitric oxide by lightning and ultraviolet rays, but more significant amounts of nitrogen are fixed as ammonia, nitrites, and nitrates by soil microorganisms. More than 90 percent of all nitrogen fixation is effected by them.

Nowadays, only a very small part of the commercial nitrogen fertilizers available are obtained from natural deposits of nitrogen salts, like Chilean saltpeter. Their main production is based on the ammonia produced by fixation of atmospheric nitrogen. The earth's nitrogen reserves are very large and the quantities of nitrogen fertilizers that can be produced from it depend mainly on the energy requirements: production of one kg of nitrogen in the form of fertilizer requires about 40 000 kJ at least, corresponding approximately to the heat of combustion of one kg of petroleum¹.

The development of fertilizers as such may be considered to have started after 1800. With the beginning of modern chemistry and a better understanding of plant metabolism and physiology, fertilization became less and less empirical. Already in 1804 Alexander von Humboldt (1769-1859) took notice of the fertilizing action of guano and saltpeter, after returning from his expedition to South America. Then, phosphate fertilizers were prepared by treatment of animal bones or (after 1840) mineral phosphate rock with sulfuric acid to make the phosphate soluble.

The first nitrogenous fertilizer to be imported into Europe was *guano*, hardened bird's droppings from islands off Perú, followed by sodium nitrate, mined in Chile, and supplemented by by-product ammoniacal solutions and ammonium sulfate from the carbonization of coal in gas works and coke ovens. In 1900 Chile provided two thirds of the fertilizer nitrogen used around the world, and in 1913 Germany bought about one-third of the total Chilean production.

By the end of the nineteenth century the demand for fertilizer nitrogen was beginning to outstrip supply and the need for man to devise methods of fixing atmospheric nitrogen was recognized and emphasized. In September 1898, Sir

William Crookes (1832-1919), in his presidential address to the British Association for the Advancement of Science, warned that supply of fixed nitrogen for agricultural purposes was rapidly reaching a point where it was insufficient to support an ever increasing population. He said that "the fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists." At the beginning of the century, a growing population placed increasing emphasis on the need to augment agricultural production by increasing nitrogen fertilizer application and considerable research was initiated to develop new processes for the fixation of atmospheric nitrogen into forms which could be used for the production of nitrogen fertilizers.

Within a few years, three different processes for the fixation of nitrogen were in commercial operation and adequate supplies of fertilizer nitrogen were assured.

In 1895 Frank and Caro were able to fix atmospheric nitrogen by the reaction of calcium carbide with nitrogen



Commercial operation started in 1915. In this process calcium carbide was heated to 1000°C in a stream of nitrogen to give calcium cyanamide, which reacted with water to give ammonia and calcium carbonate. Although the formation of calcium carbide from calcium oxide and carbon required temperatures as high as 2300 K, the overall power necessary for this fixation process was only one quarter of that required by the arc process.

In 1905, Kristian Birkeland and Sam Eyde, in Norway, started commercial production of nitric oxide, NO, by passing air through an electric arc, drawn to a sheet of flame in an electromagnetic field, with temperatures at about 3000°C . The reason for using an electric arc was that the thermodynamic equilibrium concentration of NO_2 was extremely low at atmospheric temperatures. The NO_2 was then absorbed in water forming a nitric acid solution. The nitric acid was then reacted with calcium hydroxide to form calcium nitrate containing about thirteen percent weight nitrogen, known as *Norge saltpeter*.

Both of these processes, however, were economic only where cheap electric power was available. Eventually the consumption of electricity, and hence the costs of production, were so high that made them obsolete.

The most important development of nitrogen fixation was the Haber-Bosch process for the direct synthesis of ammonia from its elements, which in 1913 was introduced on a commercial scale in Germany. This process is based on the catalytic reaction between hydrogen and nitrogen at high temperature and pressure



Haber's ammonia synthesis became the solution to nitrogen shortage and the almost ruin of Chile's nitrate industry.

In 1905 *Badische Anilin und Soda Fabrik* (BASF) began to build an ammonia synthesis plant at Oppau, in 1913 the plant initiated operations with an initial output of about 7,000 ton fixed nitrogen/year. During the period of World War I (WWI) production rose to about 60,000 ton fixed nitrogen/year. In 1918 the Haber process provided Germany with more than 200,000 ton fixed nitrogen/year.

The exploitation of salitre (sodium nitrate) started around 1810, mainly for gunpowder manufacturing purposes. The first recorded shipments of sodium nitrate from Tarapacá, then the southernmost province of Perú, took place in 1830 to the U.S., to France, and to Liverpool, England. From that year on the demand increased explosively and eventually salitre became a fundamental element for the development of agriculture at a world level and a crucial factor for the economical, social, and political development of Chile.

Industrialization of the salitre beds of the desert areas of Tarapacá and Antofagasta (today the northern part of Chile) was accompanied by a substantial migration movement to an area previously scarcely populated. The desert became rapidly populated by investors and laborers from Europe, Chile, and Perú. The difficulties caused by the presence of a large number of Chilean nationals in an area that belonged to Perú and Bolivia, and the strong economical interests involved led to the so-called "Guerra del Pacífico" (War of the Pacific; 1879-1883) that resulted in the annexation of the territory to Chile² [Crozier].

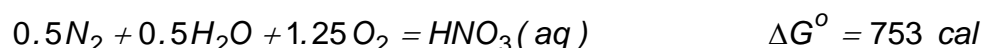
After 1830, the nitrate industry grew rapidly in response to the demand for nitrate as fertilizer, and by the time of the Franco-Prussian war (1870) annual exports had reached about 181,000 metric tons. Production continued to increase, although sometimes it was affected by natural phenomena like the Chilean 1877 earthquake, the Pacific War, periodic oversupply, and World War I (WWI). Exports reached a maximum of nearly 3 million metric tons during WWI, declined temporarily afterwards and then again increased, to the all-time high of 3.1 million metric tons of sodium nitrate (equivalent to about 511,000 metric tons of contained nitrogen) in 1928. Germany's production of synthetic nitrogen compounds, first made on a commercial scale at the beginning of WWI, surpassed that of Chilean nitrate in the early 1930s. According to Ericksen³ [Ericksen, G. The Chilean Nitrate Deposits. *American Scientist*, **1983**, 7, 366-374.] in the period 1830 to 1930, the Chilean nitrate deposits were the world chief source of fixed nitrogen for explosives, fertilizer, and a variety of chemicals. Also, from the 1870s to the mid-twentieth century they were virtually the only source of

iodine, previously extracted from seaweed. Afterwards, iodine began to be recovered from oil and gas-well brines, particularly in Japan in the USA.

The Chilean deposits never recovered their former dominance; by 1950, they accounted for only about 15% of the world market for fixed nitrogen, and in the 1990s their share was down to less than 0.1%. Resources of sodium nitrate-grade Chilean nitrate ores (at least 7% sodium nitrate) are estimated to be about 200 million metric tons, equivalent to 32.9 million tons of contained nitrogen, or less than half the world consumption in 1980. There may be several times as much lower-grade material, but that still would not be sufficient to supply world demand for more than a year or two.

The extraordinary growth in the demand for fixed nitrogen compounds since WWII has been due largely to the rapidly expanding use of nitrogen fertilizers. In 1980, global production reached 70.8 million metric tons, which is about three times the nitrogen content (23.4 million metric tons) of all the sodium nitrate produced in Perú and Chile. Today, world annual production of ammonia is more than 180 million ton/year and virtually all of this ammonia is produced from a mixture of nitrogen and hydrogen over a promoted iron catalyst operating at elevated temperature and pressure. Over 90% of the ammonia produced is used as a fertilizer, principally in the form of urea or ammonium nitrate. A significant part of new agricultural production will come from increased nitrogen fertilizer use and so the availability and source of new ammonia production will continue to be vitally important to the world's agricultural industry.

A provocative possibility for the fixation of nitrogen is the reaction



Though the ΔG° value is not attractive, the energy involved is very small so that at 20°C a 0.1 molal aqueous solution of nitric acid would be in equilibrium with the oxygen and nitrogen of the air. Lewis and Randall⁴ [Lewis, G. N., Randall, . 1923, p567] drew the attention to such a reaction saying that if a suitable catalyst could be found, all the oxygen and most of the nitrogen of the atmosphere might be used up to make the ocean a dilute solution of nitric acid. According to Goldschmidt⁵ [Goldschmidt, V. M. Geochemistry. Clarendon Press: Oxford, 1958.] this reaction could have well-taken place in the desert soil of the nitrate regions, catalyzed by one or more of the large number of rare compounds and metals concentrated in arid oxidation zones. Possible catalysts could have been compounds of vanadium, molybdenum, copper, chromium, or perchlorates, iodates, and borates. The formation of nitric acid or nitrates could have taken

place on the exposed surface of soils and rocks, with the activation energy being provided by the strong solar radiation.

Geology and geomorphology^{3,6}

Natural near-surface accumulations of nitrate-rich salts occur locally in some of the Earth's driest deserts, including the Namibian Desert in southern Africa and the Death valley region of the Mojave desert, California, but they are only abundant in the Atacama Desert located in northern part of Chile. The sources of the nitrogen present in these places and its modes of accumulation are not well understood and have been the source of lively arguments among researchers..

The global importance of desert nitrates as mineral resources has diminished, however, various types of natural occurrences are being recognized increasingly as potential sources of nitrate contamination in surface waters and ground waters in arid regions. Surficial nitrate deposits accumulated in dry climates may be leached into surface waters or ground waters when conditions become wetter, either naturally or artificially, because of climate change, flooding, waste disposal, or irrigation.

The Atacama Desert is one of the most arid regions of the world and has been so for many millions of years. Measurable rainfall (≥ 1 mm) may occur locally as infrequently as one in 5 to 20 years, and relatively heavy rains (several centimeters), as infrequently as only once or twice in a century. In the areas of the nitrate deposits, these rainfalls probably average out to an annual rate no more than 1 to 2 mm. Nevertheless, the Atacama Desert has widespread and abundant ground water that is recharged by streams and subsurface flow from the Andean Highlands. Because of this long-term aridity, the present-day landscape has changed very little since the middle Miocene.

The Atacama Desert is characterized by abundant saline minerals such as halite, gypsum, and thenardite, which occur as cementing minerals in soils, as impregnations and veins in bedrock, and as saline-encrusted playas. According to Ericksen³ [Ericksen, G. E. The Chilean Nitrate Deposits. *American Scientist*, **1983**, 7, 366-374.] "These deposits are the most unusual of all mineral deposits. In fact, they are so extraordinary, were it not for their existence, geologists could easily conclude that such deposits could not form in nature. Features of the deposit that appear to defy rational explanation are their restricted distribution in a desert characterized throughout by saline soil and salt-encrusted playas, the abundance of nitrate minerals, and the presence of other less abundant minerals containing the ions of perchlorate, iodate, chromate, and dichromate. Iodate, chromate, and dichromate are known to form under such conditions, but no chemical process acting at temperatures and pressures found at the earth's

surface is known to produce perchlorate. The nitrate deposits have exploitable quantities of iodine, an extremely high ratio of iodine to bromine, which is the reverse of the relative abundances of these two elements in other saline deposits; and the only perchlorate to occur naturally. "

The nitrate deposits are located in the two northernmost Chilean provinces of Tarapacá and Antofagasta in a band up to about 30 km wide, extending approximately from latitude 19°30' S to 26° S, a distance of about 700 km.

The most important factor in the accumulation and preservation of the nitrate deposits has been an extremely arid climate in the Atacama Desert, similar to the present nearly rainless conditions, that has persisted since the deposits began to form some 10 to 15 million years ago.

The geologic characteristics of the deposits and their mineralogical and chemical composition are roughly similar throughout the region. In the nearly rainless Atacama Desert, highly soluble salts including nitrate have accumulated in permeable regolith and fractured bedrock to depths ranging from about a meter to several meters over a relatively long period of time.

Two major types of nitrate ore can be recognized, one in which the saline minerals are chiefly a cement in unconsolidated regolith (alluvial type) and another in which they form impregnations, veins, and irregular masses in bedrock (bedrock type). The typical alluvial-type nitrate deposit is considered to be made up of five layers (a) *chuca*, of 20 to 40 cm thick, composed of barren ground, sand, and clay; (b) *costra*, (overburden) 1 to 3 m thick, made out of feldspar, calcium sulfate, magnesia, sodium, and potassium; (c) *caliche* (ore) of variable thickness, from 2 cm to several meters; (d) *coba*, a saline mixture, made of loose earth, finally granulated; and (e) *congelado*, a low-grade or barren material beneath the caliche.

Typical nitrate ore is hard and dense, and the saline constituents generally show a fine granular texture.

The relative composition of the saline components vary largely from one place to the other, gross average figures are 10% sulfate, 6.9% sodium, 6.3% nitrate, 4.6% chloride, 1.8% calcium, 0.7% potassium, 0.5% magnesium, 0.5% borate, 0.06% iodate, and 0.03% perchlorate. These constituents, which represent the water soluble material, make up an average of nearly a third of the nitrate ore, with the remainder being insoluble rock debris and saline minerals of low solubility.

Origen of the deposits^{3,6-10}

The unique nature of the salts present in the Atacama Desert and their potential commercial value has been the subject of many investigations and argument and no consensus has been reached. As we have mentioned, a number of other unusual salts such as iodates, perchlorates, chromates, and dichromates, occur with the nitrates as well as the more familiar boron, sulfate, and chloride salts. One peculiar feature of the Chilean concentration of highly oxidized compounds in the "salars" is the apparent absence of arsenates, vanadates, molybdates, and uranyl salts, which one might have expected to find. In addition, the deposits have an exceptionally high iodine/bromine ratio of greater than 10 to 1, which is the reverse of the relative abundance of these elements in other saline deposits and in rock, water, and air.

Suggested potential sources of the nitrogen in the Atacama Desert deposits include bird guano, fixation of atmospheric nitrogen during electrical storms and electrochemical and photochemical reactions in the atmosphere, leaching of Andean volcanic rocks, organic-rich sea spray, atmospheric fallout of marine-derived nitrate, microbial nitrogen fixation in the desert soils and playas, and ascending hydrothermal fluids.

The many hypotheses on the origin of Chilean deposits have been discussed by Goldschmidt⁵ [Goldschmidt, V. M. *Geochemistry*, Oxford, Oxford, 1958.], who suggested that because Chilean nitrates contain approximately 0.2% iodine as iodate, a solution to the problem of origin of these deposits may be found if the presence and state of oxidation of iodine compounds in salts deposits in other parts of the world were studied.

According to Ericksen⁸ [Ericksen, G. E. *Meditations on the Origin of the Chilean Nitrate Deposits*. Open File Report, 86-361; U. S. Geological Survey, Reston, VA.] the nitrate deposits of Chile owe their existence to an environment favorable to the accumulation and preservation of the deposits rather than to any unusual source of the saline materials. Most of the nitrate was fixed by soil microorganisms and lesser amounts were fixed by photochemical and electrochemical reactions in the atmosphere while most of the other saline constituents probably are of volcanic origin, occurring chiefly as soluble saline material, but an unknown amount is of oceanic origin, having been carried inland as windblown particulate matter and, perhaps, in fog-droplet solutions. Most of the saline material now in the Atacama Desert was first deposited in ephemeral lakes and salars, from which it was eroded by the wind and spread widely throughout the desert.

On the basis of his many studies of the Atacama Desert^{3,6-10}, Ericksen has proposed the following theory for their origin^{8,9} [ref]:

(a) The deposits formed chiefly during the later Tertiary and Quaternary time, the last 10 to 15 million years, when intervals of slightly greater rainfall in the Andes provided runoff for several ephemeral lakes and ponds in the Atacama Desert. These bodies of water probably were characterized by shallow stagnant saline waters having abundant microorganisms. Microorganisms should also have been abundant in the moist soils in flat areas marginal to former lakes and ponds and in solids exposed to annual fluctuations in lake levels.

(b) Dry saline material from ephemeral lake beds and nearby soil surfaces was picked up by the wind and carried to the sites of the nitrates deposits in nearby areas.

(c) The chief sources of the ordinary saline constituents (sulfate, chloride, sodium, calcium, potassium, and magnesium) were water soluble materials in the volcanic rocks of the Andes, which were leached by rainwater and carried into the Atacama Desert by streams and ground water.

(d) The nitrate is probably chiefly of organic origin, consisting of atmospheric nitrogen fixed by soil microorganisms. Nitrogen is known to be fixed in nature by microbial activity in soil and water, by photochemical and electrochemical reactions in the atmosphere, and by volcanic-gas reactions. Most of the nitrate in the deposits probably formed by fixation of atmospheric nitrogen by photoautotrophic blue-green algae in the synthesis of organic compounds, chiefly protein. Decay of these compounds and action of ammonifying bacteria first release ammonia or ammonium, which in turn is transformed to nitrate by nitrifying bacteria.

(e) Windblown saline material at the sites of the deposits was reworked by water from the infrequent rains to rearrange some of the saline constituents according to solubility, bringing about enrichment of nitrate at deeper soil levels and lower hill slope levels.

(f) The nearby Pacific Ocean and Humboldt current may have played a role in the formation of the nitrate deposits, but their importance is difficult to estimate. Perhaps most important is the prevalent winter fog or *camanchaca*, which is due to temperature inversion caused by the cold Humboldt current. The considerable condensate supplied to the soil may have promoted activity of soil microorganisms, including nitrogen-fixing forms. The Humboldt current also is a potential source of iodine that concentrates in organic films on the sea surface,

films that are ejected into the atmosphere in bubble spray. Bubble spray may also be a source of ammonium that was transformed to nitrate.

Recently, the available information has been supplemented by isotopic studies. According to Böhlke et al.¹¹ [Böhlke, J. K., Ericksen, G. E., Revesz, K. *Chemical Geology* **1997**, 136, 135-152.] analyses of samples from Chilean nitrate deposits indicate that the nitrate nitrogen is slightly depleted in ^{15}N with respect to atmospheric nitrogen, which is in contrast to most organically-derived nitrogen in soil, sediments, ground waters, and surface waters that are more commonly enriched in ^{15}N . Values of $\delta^{15}\text{N}$ near 0% are consistent with either bulk N deposition or microbial N fixation as major sources of the nitrogen in the deposits. In addition, $\delta^{18}\text{O}$ values range from +31 to 50‰, significantly higher than those of atmospheric oxygen (+23.5 ‰). Such high values of $\delta^{18}\text{O}$ are considered unlikely to result entirely from nitrification of reduced nitrogen, but rather resemble those of modern atmospheric nitrate in precipitation from some other localities.

A preliminary petrographic study of the Chilean nitrates has lead Searl and Rankin¹² [Searl, A., Rankin, S. *Geol. Mag.* **1993**, 130, 319-333.] to conclude that the ore composition reflects the derivation of precipitating fluids from a variety of sources: westward flowing Andean ground water, coastal fogs, occasional rainfall, and Andean-derived surface floodwaters. The unusual mineralogy of the nitrate ore reflects the extreme chemical evolution of the precipitating nitrate brines through multiple stages of salt precipitation and remobilization during transport to the nitrate fields. The formation of high purity nitrate ore appears to be the results of highly soluble nitrate salts from less soluble salts in the overlying profile.

Precipitation and dry deposition from the atmosphere (including aerosols, rain, snow, fog condensation, and dew) may be significant sources of nitrogen-bearing salts in deserts^{13,14} [Claridge, G. G. C., Campbell, I. B. Origin of Nitrate Deposits. *Nature*, **1968**, 217, 428-430. West, N. E. Physical Inputs of Nitrogen to Desert Ecosystems; Chapter 11 in Nitrogen in Desert Ecosystems, N. E. West and J. Skujins, eds., U.S. International Biological Synthesis Series, vol. 9, Hutchison and Ross: Stroudsburg, 1978; pages 165-170.]. $\delta^{15}\text{N}$ values for nitrogen compounds in rain and atmospheric matter are variable but commonly average less than approximately equal to 0‰. Ammonium and nitrate derived from in situ degradation and oxidation of animal wastes, including bird guano, almost invariably have $\delta^{15}\text{N}$ values significantly greater than 0‰. Thus, the nitrogen isotope data for the caliche-type desert nitrates indicate that they probably are not oxidized residues of animal wastes.

Wind-transported sea spray containing organic-rich surface films has been considered as a possible source of iodine and nitrogen, both of which are uniquely abundant in Chilean nitrate deposits. However, the majority of reported $\delta^{15}\text{N}$ values for marine nitrogen-bearing substance such as plankton, zoo plankton, dissolved ammonium, nitrate, and particulate organic nitrogen are significantly greater than 0‰. It is not clear that these substances would be preferentially released from the ocean and transported to the continents.

The conclusions of Searl and Rankin have been severely criticized by Ericksen claiming that they are based on assumptions that are partly or wholly in error, particularly the one on the amount or effect of the local rains. According to Ericksen rainwater leaching is a long term process that has played an important role in the accumulation of nitrate ore. The existence of high grade ore that occurs in the Chilean deposits is the result of leaching of highly soluble saline materials located at the surface, followed by their re precipitation at deeper levels⁹ [Ericksen, G. E. Discussion of a Petrographic Study of the Chilean Nitrates - Comments. *Geol. Mag.* **1994**, 131, 849-852.].

According to Claridge and Campbell¹³ [Claridge, G. G. C., Campbell, I. B., Origin of Nitrate Deposits. *Nature*, **1968**, 217, 428-430.] the proportion of iodate to nitrate in the Antarctic salts is similar to that in the Chilean nitrate deposits; consequently, it seems likely that the nitrates and iodates are genetically related and have a similar origin in both the Chilean and Antarctic deposits. Since the atmosphere contains small quantities of nitrogenous material as well as compounds of iodine, sulfur, and chlorine derived from the ocean surface, in various proportions and states of oxidation, they form part of the precipitation from the atmosphere. Garrett has criticized the hypotheses of atmospheric fallout out of ocean spray pointing out some of the minerals in the nitrate deposits have been reported in atmospheric gases, but not all of them. Similarly, minerals contained in seawater, such as bromine, are either non present or present in the wrong proportions. According to Garrett the accumulation of iodates and perchlorates was caused by reactions driven by photocatalysis¹⁵ [Garrett. D. E. Chemistry and Origin of the Chilean Nitrate Deposits. Sixth International Symposium on Salt. Salt Institute. vol. I, 1983.]

Development of the nitrate fields and the production process

There are numerous evidences in the old literature that the Indians of Southern Perú were well aware of the existence of caliche and its fertilizing properties. They would grind it very finely and add it as fertilizer for their crops of wheat, corn, and potatoes, the same as they did with guano. According to Donald¹⁶

[Donald], another strong indication is that a *Quichua* dictionary published in 1604 by Padre Maestro Fray Juan Martínez contains an entry for salpetre (*collpa çuca*) and another for nitrate grounds (*collpa, collpa, çuca*). Many documents dated 1713 and 1756, during the time of the Spanish Conquest give testimony that the miners working in the South of Perú had already realized that they could extract from the soil a material that could be used instead of potassium nitrate to manufacture gunpowder to help them in the mining processes. This was done in spite it being prohibited by the Royal authorities to protect the royal monopoly of its fabrication. For example, there is a 1571 royal order of King Felipe II (kept in the archives of *Leyes de Indias*), expressing that "we prohibit the manufacture of gunpowder everywhere in the Indias, without permission of the governor or the authorities of the city in which it is desired to manufacture it". In 1628 the limits of the *corregimientos* of Arica, which included the Tarapacá nitrate fields, were defined by boundary stones. As stated in a later document (1846) the original line of demarcation passed from Tocopilla on the coastline eastwards to the Andes and contained the two boundary marks named "the three mount on the nitrate plain" and "in the lone nitrate plain"¹⁷[Hernandez].

There is also a copy of an edict issued by the Colonial government at the start of Perú's War of Independence (1821-1824), that prohibited the exploitation of the caliche fields to avoid its being used by the rebels for manufacturing gunpowder¹⁸ [Kaempfer, E., *La Industria del Salitre i del Yodo*. Imprenta Cervantes: Santiago, 1914.].

According to a popular legend, the salitre beds of Southern Perú were said to have been discovered accidentally by two Indians who after a hard day of work camped in the pampa and started a campfire to warm themselves. All the sudden they saw that the ground started to burn and ran away thinking that they had seen the Devil. Later on they told what happened to the priest at Camiña who then went to the spot, took a sample of the ground, had it analyzed, and found that it contained sodium nitrate. According to the legend, the priest threw the rest of the ground on the courtyard of his house and observed that the plants developed vigorously thanks to the fertilizer they had received. After this observation the priest recommended to his faithful the use of the material as an "excellent tonic for the plant kingdom."^{16,19} [Bollaert, W., *Antiquarian, Ethnological and Other Researches in New Granada, Equator, Peru, and Chile, with Observations On the Preincarial, Incarial and Other Monuments of Peruvian Nations*. Trübner & Co: London, 1860.][Donald, M. B. *History of the Chilean Nitrate Industry*.-I. Ann. Sci. (London), 1936, 1, 193-216.].

Additional evidence that caliche was known by the Spaniards as a good raw material for gunpowder is the contract that the Viceroy of la Croix signed with

Antonio Bohorquez at the end of the 18th century, to manufacture gunpowder at the price of 3.5 *reales* per pound of military quality and 2.5 *reales* per pound of mining quality. Sometime afterwards, Lucas Rodríguez de Molina invented in Lima a new machine for the manufacture of gunpowder using the salitre from Tarapacá. This gunpowder was of such a good quality that the King of Spain rewarded the inventor with a coat of arms¹⁷ [Hernandez].

In 1792 the Peruvian writer Manuel de Mendiburo, gave the following description of the procedure used by the natives for purifying it for the manufacture of gunpowder: "The Indians removed the crust of the earth, crushed into small pieces, and allowed it to soak for 24 hours in water contained in a cow skin shaped like an inverted cone, with a wooden plug at the bottom outlet. The liquid was removed and boiled in kettles for one hour, and then left standing in vessels for 24 hours, whereby the nitrate separated as dirty-colored crystals. These were purified by redissolving in water and adding a beaten up egg and then strained through cloth into glazed earthen ware receptacles." The nitrate so obtained was converted into gunpowder and used in the nearby cinnabar mines at Huancavélica, which had been started in 1564. Indians also used the powder for fireworks until this practice was prohibited¹⁶ [Donald, M. B. History of the Chilean Nitrate Industry.-I. *Ann. Sci.* (London), **1936**, 1, 29-47.].

A report published in 1803 by Juan Egaña, Secretary of the Royal Court of Mines of Chile, indicated that the Huasco region was "covered in a large part by a crust of niter salt, well crystallized, and several inches thick." In this report the word caliche is defined as "an efflorescent, or pyrites containing substance, which looks as lime and which contains silver." Similarly, the Peruvian newspaper, *Minerva Peruana*, carried on June 15, 1809, a piece informing the "discovery in Tarapacá of a very large bed of nitrate of soda, so large that it can provide all the Americas and Europe."¹⁷ [Hernandez]

Charles Darwin (1809-1882) visited Iquique on July 13, 1835, on board H.M.S. Beagle and paid a visit to the nitrate works. In his *Journal of Researches*²⁰ [Darwin, C. Journal of Researches into the Geology and Natural History of the Various Countries Visited by H.M.S. Beagle; 1839.]; he says: "The mine consists of a hard stratum, between two to three feet thick, of the nitrate mingled with a little of the sulfate of soda and a good deal of common salt. It lies close beneath the surface and follows for a length of 150 miles the margin of a grand basin or plain."

All the sources agree that Thadeus Haënke (1761-1817) is the one that took the first step toward the commercial development of the nitrate fields. Haënke was born at Kreibitz, Bohemia, and educated at the Universities of Prague and Vienna. In 1795 he established himself in Cochabamba, Bolivia, where in 1798

he wrote the book *Natural History of Cochabamba*. In this treatise, under the entry nitrate of potash, he wrote: "I should observe that as a thing very rare in chemistry and mineralogy one finds abundantly in this country native cubic nitre (nitrate of soda), which is very rarely found in the old continent." Under the entry mineral alkali or native soda, he wrote: "This salt is found in great abundance all over the Kingdom. The extensive nitrate fields, which are traversed in the routes that follow the coast in the districts of Tarapacá, Moquegua, Caman, and Atacama, are composed chiefly of this substance." A particular contribution of Haënke to the development of the salitre industry was his procedure to convert sodium nitrate into potassium nitrate. Haënke's procedure consisted in adding to the salt solution a lye prepared from burnt cactus (which contained about 8% of potash)¹⁹ [Bollaert].

Development of the exploitation process

The primitive nitrate works were known as "*paradas*"; its central units were the dissolving tanks or "*fondos*", one-meter deep cone-shaped vessels made of wrought iron, having their largest diameter some 1.5 meters and a capacity for nearly a ton of the raw material or caliche containing 50-60% of sodium nitrate. The tanks (usually two, hence the name *parada*, from the word pair) were heated directly by fire provided by the burning of fossil wood that was dug up in the Pampa of Tamarugal. The hot liquid was run off into crystallizing tanks or "*bateas*" made of wood or iron and fixed in such a position that the liquor could easily flow into them from the tanks. The essential concept in the purification process was that at high temperatures (near the boiling point of water) the nitrate is very much more soluble than the salt, and that the hot liquid on cooling deposited almost pure sodium nitrate; the salt and other impurities remained in the residue or "*ripio*" in the tank. An important disadvantage of the "*parada*" was that it required caliche of very nitrate content with the resulting transportation expenses.

The crystallization process lasted about 12 hours; after filtration the mother liquor was accumulated in especial tanks and used for treating the following batches of raw mineral. The wet crystals were then put to dry in the sun. In some cases an intermediary settling tank, or "*chullador*", was used to allow the mud and slime to settle from the hot solution: an operation that diminished the salt content. The process was highly inefficient, it recovered about 50% of the sodium nitrate present in the original ore. Most of the losses were due to inefficient blasting of the caliche bed and to the extraction residue remaining with about 10 to 15% nitrate. Poor blasting resulted in the bed becoming covered with debris, forcing the miner to move to another location.

This process was the basis of several plants built in Zapiga, east of the city of Pisagua. Their largest production was between 1809 and 1812 when they manufactured a total of 1140 tons de nitrate that was shipped to Lima to be used in the manufacture of gunpowder.

The primitive process was improved several times. In 1853 Pedro Gamboni, in 1853, replaced heating by direct fire by steam injection directly into the cooking vessel, and in 1876 Santiago T. Humberstone (a British chemical engineer that moved to Chile in 1875) used indirect steam heating.

Gamboni dissolved the caliche in rectangular tanks, 7 m long, 2 m wide and 2 m deep, that had a perforated plate or "*crinolina*" placed just above the bottom of the tank. Steam, generated in Cornish boilers, was blown into the tanks by means of perforated pipes situated under the crinolinas. The procedure consisted in charging the tanks with caliche and mother liquor followed by steam injection into the load. The density of the solution would gradually rise, and then it would start to fall owing to dilution by the condensed steam. This was considered to be the end of the operation; the hot liquors were then drained into the crystallizing tanks. Each batch operation was known as a "*fondada*" and the average production per tank was four fondadas per day. Direct injection of steam into the bed produced large amounts of mud, which made leaching and filtration difficult. Anyhow, Gamboni's method resulted in a faster dissolution of the nitrate, a better use of energy, and an increase in capacity of more than ten times that of the "*parada*"¹⁶ [Donald I].

(a) *The Shanks process*²¹ [Donald II]

Several factors led to the next development stage (a) Natural wood became scarce and imported carbon begun to be used as fuel, with the corresponding increase in costs, (b) increased awareness of the fertilizing properties of sodium nitrate led to its larger and larger use in Europe and, (c) the Crimea War (1853–1856; between Russia, England, France, and the Ottoman Empire) led to a very large additional demand for gunpowder, and, (d) the decreasing nitrate content in the ore.

The "*paradas*" system, including the Gamboni improvements, was unable to satisfy the increased demand and resulted in its substitution by the Shanks process.

Along with indirect heating, Humberstone also adopted the countercurrent lixiviation process developed by Shanks²² for obtaining soda ash using the Le Blanc process [Shanks, J. Brit. Pat. 3232, 1863.] . The Shanks procedure resulted in significant economy, not only in the amount of fuel used but also in the maintenance of the steam boilers, because now the condensate was returned to

the boiler, with the corresponding decrease in fuel requirement, and also in the amount of scale formed in it, since the water used was not replaced by highly saline fresh water. In the Shanks countercurrent lixiviation process the tanks were connected in series, the solution that permeated to the bottom of one vessel was then pumped to the head of the following tank, and so on. The liquid from the last element in the series was returned to the head of the first one. When the first vessel of the series became exhausted, the next vessel became the head of the series, while the previous one was emptied and recharged with fresh raw material.

The expansion of the industry that took place after the Pacific War led to the need to exploit caliche beds of lower and lower nitrate content. The Shanks process allowed using caliches containing as little as 15% sodium nitrate, as compared with the 50% content required by the previous processes. For example, its introduction in the plant *San Antonio* resulted in an increase in production from 870 to 1300 tons per year and a parallel reduction of 50% in water and fuel expenses. In addition it allowed reducing the lixiviation temperature from 80°C to 60°C.

The Shanks process consisted in blasting the desert salitre bed, grinding the rock and charging the ground raw material into the "cachuchos", which were tanks made of wrought iron and provided with internal heating coils fed with steam from the boilers. Leaching was done at 70°C with a solution consisting of water and a mother liquor brine containing about 450 g/L sodium nitrate, and increased the concentration to 700-750 g/L. The saturated sodium nitrate solution was then clarified by sedimentation in iron tanks ("chulladores") and then pumped into a preliminary cooling pan where temperatures were allowed to drop to about 25°C to precipitate sodium chloride. The slime was allowed to settle after addition of a coagulant such as wheat flour. The clear liquor was transferred to the nitrate crystallizing pans and allowed to cool overnight to ambient temperature. The remaining liquid was used for manufacturing other products such as iodine and borax. The lixiviation solid residue (ripio) was removed and conducted to the disposal ground ("torta de ripio").

The Shanks process had some additional technical and economical advantages over the processes used previously, for example,

(a) Crushing of the raw caliche resulting in the production of some very finely divided material, containing large amounts of clay and sand. The practice adopted was to separate the larger particles from the fines and treat each separately.

(b) Higher leaching efficiency was usually obtained by increasing the amount of fresh water used in the leaching cycle. The amount of water that could be employed was dependent upon the amount of water lost in the process.

In 1928 the Shanks process was yielding a leaching efficiency of about 83% on a caliche containing 16% of sodium nitrate. Fuel consumption was about 0.154 tons of fuel per ton of NaNO_3 . The new process resulted in a tremendous economic boom with more than 300 plants operating all over the desert. As a consequence, the salitre industry became the principal economic activity in Chile.

The Shanks process remained in use until 1977 when the last plant using it was closed.

Further improvements were realized by a better understanding of the phase diagram of the system. Measurements indicated that at 20°C one kg of water could dissolve either 890 g of NaNO_3 or 367 g of NaCl . A saturated solution of both solutes was shown to contain 570 g of NaNO_3 and 260 g of NaCl . The solubility of NaNO_3 in water varied with temperature substantially more than that of NaCl , at 100°C one kg of water dissolved 1690 g of NaNO_3 or 397 g of NaCl ; the same amount of water saturated in both solutes contained now 1575 g of NaNO_3 and 160 g of NaCl . In other words, heating a solution saturated in both compounds from 10° to 100°C resulted in the solution of an additional 685 g of nitrate and precipitation of 100 g of chloride. Using these results, it was possible to produce the partial crystallization of the salts by gradual cooling, and to separate NaNO_3 essentially pure¹⁸ [Kaempfer].

Little by little the complex salt system began to be understood and solubility phase diagrams of the principal components begun appearing in the literature^{23,24} [Cretien, Cornec].

(c) *The Guggenheim system*

The Guggenheim process, introduced in the late 1920s, allowed treating ore of grade as low as 7% NaNO_3 , making it possible to mine it by mechanical means, instead of manually. Furthermore, this lower grade ore could be leached with only slightly warm solutions ($35\text{-}40^\circ\text{C}$) as opposed to the boiling solutions required for high grade ore. The nitrate was precipitated by refrigeration, replacing the process of evaporation and cooling in open tanks. The sodium nitrate could be as high as 450 g/L, which was more than 50% of the total dissolved solids, and could be easily removed by crystallization by cooling to about 15°C . The recirculation system recovered more than 75% of the nitrate. Addition of salts like magnesium and calcium sulfates helped decomposing the soluble double salt darapskite $\text{NaNO}_3\cdot\text{Na}_2\text{SO}_4\cdot\text{H}_2\text{O}$ present in the caliche, thereby increasing

NaNO_3 extraction. In the Guggenheim process, astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) precipitates instead of darapskite.

The process used nowadays is basically the same as the original one, except of modifications introduced to recover additional salts of commercial value such as potassium nitrate, sodium sulfate, sodium potassium nitrate, potassium chloride, borates etc. Leaching is carried at 40°C using a mother liquor entering the process with 320 g/L and leaving with 450 g/L. Crystallization is effected in shell-and-tube heat exchangers, using ammonia refrigeration; the crystals are separated by centrifugation. The fines produced by the crushing process (about 25% in weight) are sent to washing tanks for the extraction of iodates, and eventual recovery of iodine. The mother liquor of nitrate crystallization is also stripped of iodates before being returned to the lixiviation tanks.

The Guggenheim process has increased mechanization. Steam shovels load the caliche into cars that are hauled by electric locomotives to the crushers. After the caliche has been pulverized it is carried on conveyor belts into the vats and conducted through four vats in the same manner. The extraction liquors are heated to $35\text{--}40^\circ\text{C}$ by means of the exhaust gases from the Diesel engines used for supplying power to the plant and the electric trains.

By the end of the 20th century the world wide production of sodium nitrate was about 520,000 tons/year, of this 450 000 (86%) were produced in Chile.

The rise and fall of the economic dream²⁵

The first shipment of caliche was from Tarapacá to Concepcion (in the South of Chile), before the year 1800, as an alkali raw material for the manufacture of soap. In March 1830 the Government issued a decree authorizing the export of salitre, and requiring the exporters to pay all the expenses related to the travel and lodging of the customs officers that had to travel North to authorize the shipments. The first shipments went to the U.S., to France (used for the manufacture of gunpowder by the followers of Louis Phillip d'Orleans after the Restoration), and to Liverpool, England. The latter shipment was a failure and the nitrate was thrown overboard into the sea. Different sources gave different reasons for this action, one, that the price was not attractive, another that the excise duties were too high, and the third, that the Port captain did not allow the boat to come in because it was carrying a dangerous load. Anyhow, a few bags were distributed among some farmers of Glasgow, who used it as a fertilizer and reported a three-time increase in crop yield. In 1833 a Dutch publication indicated that "the principal use of this nitre in Europe is manufacturing rockets and fireworks for saint day displays in Catholic countries. Western Perú

furnishing nothing but the precious metals to make the return trip to England in payment of manufactures, hence this nitre was immediately hailed as a great boon to the returning ships by furnishing them with a profitable ballast."

The most significant event in the development of the industry was not technological but political. Chile defeated Perú and Bolivia in the Pacific War and took as indemnity their nitrate lands, thus becoming the sole owner of the world's only known deposits of nitrate of sodium² [Crozier].

Salitre exports resulted in a huge income of hard currency for Chile. By 1837 exports had grown to 6 900 ton/year, of which two-thirds went to England and the rest to France. By 1850 exports had risen to about 24 000 ton/year, in 1910 they were 2.4 millions tons/year per years, and by 1916 they had reached 3 million ton/year, produced by 97 plants. The boom was so large that salitre became known as the "white gold". The State income from salitre exports reached almost 60% of its total income.

There is no argument that salitre was a fundamental element for the development of agriculture at the international level, as well as a crucial activity for the social, economic, and political development of Chile. For example, almost 55% of the private railroad tracks were located in the northern provinces. It was also instrumental in the demographic distribution, the cities in the North of Chile had grown from a few hundreds to population sizes as the main cities in the center of the country.

More spectacular yet is the fact that Government income from salitre and all related activity was so high that citizens were exempt of paying taxes! The Government was charging the manufacturers a tax of \$ 0.58 per kilogram salitre, an amount almost equal to the cost of production per kilogram (ES ESTO CIERTO? O CUAL ES LA VERDADERA CIFRA).

Introduction of the Shanks technology resulted in a 145% increase in exports, construction of more and more plants and a large migration of workers to the North of Chile. Some towns went from an initial population of about 100 to over 10,000. At the peak of the activities more than 30,000 workers were involved in the production of salitre.

The first serious blow to the nitrate business came in 1914 when Germany, which was buying the largest share of Chilean nitrates, was cut off by the outbreak of WWI and began manufacturing ammonia and its derivatives. At the onset of the war the number of Chilean nitrate plants in operation fell from 134 to 43. During the war the Allies replaced Germany as nitrate consumers and Chilean exports increased rapidly; 1917 was the best year the industry had. After the war, gunpowder requirements returned to usual and resulted in another serious decrease in business. In 1919 exports fell to the lowest point in volume

since 1892 (804 ton/year). Thereafter production took an erratic course varying in the following ten years between one to three million tons per year, with the corresponding effects in unemployment and social unrest. More significantly for the future, the Shanks process had gone from a very attractive alternative to an uneconomical one. Of the 140 plants available, only 43 were operating regularly. The rest of them would open and close according to the whims of the market.

In global terms, in 1913 the salitre production supplied 54.7% of the world consumption of nitrogen; by 1923 the figure had gone to 32.2%. The worldwide economic depression of the 1930s made things worse and sent the salitre industry into the worst slump of its history, The Chilean government become deprived of the major part of its revenue and found it difficult to meet the service requirements on the foreign debt. By 1978 only four operating facilities were left, many of the original producing sites and their accompanying living quarters had become ghost towns for tourist to visit.

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