A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR -86-1363

RECEIVED BY OSTI MAY 12 1986

CONF-860437--1

TITLE: THE NON-ENDING HELIUM STORY

LA-UR--86-1363

DE86 010192

AUTHOR(S): E. F. Hammel, M. C. Krupka, K. D. Williamson

SUBMITTED TO: ICEC11 - Eleventh International Cryogenic Engineering Conference
West Berlin, April 22-25, 1986

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

THE NON-ENDING HELIUM STORY

E. F. Hammel,* M. C. Krupka and K. D. Williamson, Jr.

Los Alamos National Laboratory, Los Alamos, NM, USA

Why an adequate supply of helium is of importance to cryoengineering is obvious to everyone present at this conference. Why there is a non-ending helium problem - or more specifically why helium supply problems have arisen in the past, why they may arise again in the future, what are those problems and what solutions appear to exist - is more complicated. To answer these questions this paper is divided into three sections: resource availability, the demand for helium and the supply of helium.

Helium was first found to exist on earth by Sir William Ramsey[1] in 1895 among the gases released from a radioactive mineral upon heating with sulfuric acid. Later in that same year, helium was discovered by H. Kayser[2] to be a component of the natural gases evolving from a Wildbad spring in the Black Forest. This discovery immediately suggested that helium ought also to be a component of the atmosphere and this expectation was confirmed in Kayser's same 1895 paper. Since these initial discoveries, helium, in volume per cent concentrations up to 16%, has been found in natural gases throughout the world. Unfortunately, however, the estimated total amount of helium in these very high concentration reservoirs has turned out to be negligibly small. It was not until 1905 that H. P. Cady[3] of the University of Kansas identified helium as a component of the gas contained in a large natural gas reservoir in Dexter, Kansas. The concentration of helium in that gas was almost 2%. Despite the discovery that relatively large and rich terrestrial resources of helium existed, only small amounts of the gas were produced (primarily for scientific investigation) during the next decade. The first efforts to produce helium in large quantities from natural gas were initiated in Canada in 1915 and in the United States during 1917 for military use in lighter-than-air craft: observation balloons, barrage balloons and dirigibles. Although these efforts were successful in demonstrating the technical and economic feasibility of large scale helium production from so-called helium-rich (>0.3 vol.%) natural gases, the November 11, 1918 Armistice occurred before enough of the gas had been produced to permit its utilization. From a practical standpoint, however, it had been demonstrated by the first quarter of the 20th century that helium could be produced in large quantities and at reasonable cost from helium-rich natural gases and it had also been discovered that, through some quirk of nature, most of the world's supply of high helium concentration natural gases were concentrated in the southwestern portion of the United States. From a more general standpoint, the world resource situation with respect to helium is summarized in Table 1.

Since the present world annual consumption of helium ($2x10^9$ cf or $6x10^7 m^3$) is only 10^{-5} % of the world's helium resources, it would seem at first sight that no helium supply problem could possibly exist. Unfortunately, this conclusion is incorrect

*Consultant to the Los Alamos National Laboratory and, to understand why it is incorrect, it is necessary to examine more closely the technical and economic feasibility of extracting helium from each of these terrestrial categories.

The quickest and easiest category to dispose of is the hydrosphere. Despite the fact that it contains about one thousand times the world's current annual production of helium and despite the fact that the source material is uniform in concentration and easily accessible, to obtain $3x10^7$ m^3/yr of helium from the hydrosphere would involve processing annually (with 100% extraction efficiency) an amount of sea water equivalent to about 1/3 of the Mediterranean Sea!

A second category, the atmosphere, is also characterized by easy accessibility and a uniform helium concentration. In addition, the extraction technology is already developed and hence available. The primary problem with atmospheric extraction is, however, analogous to that which precludes serious consideration of hydrospheric extraction, namely the immense amount of the source material that must be processed. With a helium concentration in air of only 5 ppm, approximately 200,000 volumes of air must be treated (again at 100% extraction efficiency) to yield 1 volume of helium. Although it will be costly to produce helium from the atmosphere, exploitation of this source may ultimately become necessary.

The last major category to consider is the lithosphere, generally defined as the earth's "crust"* plus the upper rigid portion of the mantle. The surface separating the rigid portion of the mantle from the plastic portion is called the Mohorovicic, or Moho, discontinuity. Approximately 96% of the earth's helium inventory resides in the lithosphere and of that, about 95% is believed to be trapped in the crustal igneous rocks. The helium content of these rocks seldom exceeds about 10^{-7} cm^3/g, although much higher concentrations have been confirmed in radioactive mineral deposits such as sandstone U_3O_8 ores (~0.03 cm^3/g), thorianite (3.5-10.5 cm^3/g), monazite (0.8-2.4 cm^3/g), etc.

A little arithmetic shows that the extraction of amounts of helium from ordinary igneous rocks would be hopelessly expensive. For example, to obtain from that source the present world annual consumption of helium would involve processing with 100% extraction efficiency about 200 km^3 of rock per year (equivalent to a rock cube 6 km on a side).

About a decade ago two of the present authors (E.F.H. and M.C.K.) examined the feasibility of collecting the helium released during uranium mining operations. Admittedly, uranium ores contain less helium than other radioactive minerals, but in this case the mining, milling and leaching processes are carried out to obtain the

... is called the Mohorovicic, or Moho, discontinuity. Approximately 96% of the earth's helium inventory resides in the lithosphere and of that, about 95% is believed to be trapped in the crustal igneous rocks. The helium content of these rocks seldom exceeds about $10^{-[illegible]}$ cm^3/g, although much higher concentrations have been confirmed in radioactive mineral deposits such as sandstone U_3O_8 ores (~0.03 cm^3/g), thorianite (3.5-10.5 cm^3/g), monazite (0.8-2.[illegible] cm^3/g), etc.

A little arithmetic shows that the extraction of amounts of helium from ordinary igneous rocks would be hopelessly expensive. For example, to obtain from that source the present world annual consumption of helium would involve processing with 100% extraction efficiency about 200 km^3 of rock per year (equivalent to a rock cube 6 km on a side).

About a decade ago two of the present authors (E.F.H. and M.C.K.) examined the feasibility of collecting the helium released during uranium mining operations. Admittedly, uranium ores contain less helium than other radioactive minerals, but in this case the mining, milling and leaching processes are carried out to obtain the uranium; hence by-products, such as helium can be recovered relatively inexpensively. We found that, for an ore containing approximately 0.2% U_3O_8, the maximum amount of helium that could be extracted was about 1 cf/ton (0.03 m^3/metric ton). During the mid-1970's, in the heyday of the uranium mining industry in the US, production had reached about $10^{[illegible]}$ tons of uranium ore per year. But even then, had all of the helium released during the milling and leaching processes been recovered, the total production from this source would have satisfied less than 1% of demand. Today the percentage would be much smaller. Since, of all of the radiogenic ores, only those containing uranium are being mined in relatively large quantities, since these quantities are capable of providing only a trivial amount of by-product helium (compared with world demand) and since the cost of mining and processing radiogenic ores which are richer in helium only for their helium content would be prohibitively expensive, it appears that igneous rocks are most unlikely to be utilized as a future source of helium.

Helium is constantly being created in the lithosphere by radioactive decay processes at a relatively constant rate (for example, the half life of uranium is about

---

*The earth's crust consists, under continents, of a layer of granitic rocks below which is another layer of basaltic rock; this basaltic layer extends outward from the continents and forms the floor of the oceans.

4.5×10^9 years and that of thorium is three times longer. But, due to the action of water, seismic activity, other weathering forces and the fact that some rocks are much more porous to helium than others, helium is constantly escaping from the lithosphere to the atmosphere and from there to outer space. Hence the concentrations of helium in the lithosphere, the hydrosphere and the atmosphere all remain essentially constant (and have remained so for millions of years) because of these steady state generation and loss processes.

In addition to the helium resident in igneous rocks, substantial amounts also exist in trapped pockets of natural gas. A specification of this resource estimate for helium from the available data is, however, not simple since many different varieties of natural gases exist. Fortunately, for our purposes, it is adequate to note that commercially producible amounts of helium exist primarily in natural fuel gases and the world's economically producible natural fuel gas reserves and still-to-be-discovered resources are currently estimated at about 10^{16} cf (3×10^{14} m^3).[5] If one assumes that the average concentration of helium in this gas is about 0.05 vol.%,** the amount of helium resident in these gases is about 5×10^{12} cf (1.5×10^{11} m^3). In our discussion of the helium content of the several components of the lithosphere, nothing even remotely resembling a material balance has been achieved. If 95% of the lithospheric helium is trapped in the igneous rocks, where is the remainder? Certainly not in the natural fuel gases. The missing fraction is probably to be found in helium trapped in sedimentary and metamorphic rock formations, in coal and/or coal seams and in so-called unconventional natural fuel gas sources such as the methane hydrates, tight gas formations and geopressured reservoirs. In addition, primordial helium has been identified as a component of abiogenic natural gases emerging from deep ocean trenches, volcanic gases, and rift zone seepages. Nonfuel (or low-Btu) natural gas fields containing substantial amounts of helium have also been discovered. Because the gas from these reservoirs cannot be utilized as a fuel gas without first removing the noncombustible components of the mixture (a costly process) these exploratory wells have, for the most part, been cemented shut and abandoned. Finally, although exploration of the earth's crust for natural gases has resulted in the drilling of millions of exploratory and producing wells, practically all of these wells have been less than two kilometers deep. In certain areas, however, substantial gas deposits have been discovered at greater depths and it is possible that more natural gas (and probably more helium as well) will be discovered in the future as this next deeper layer of the lithosphere is explored. In other words, the helium resource story is still being written.

THE DEMAND FOR HELIUM

At present, at least three quarters of the wo ld demand for helium is being reservoirs. In addition, primordial helium has been identified as a component of abiogenic natural gases emerging from deep ocean trenches, volcanic gases, and rift zone seepages. Nonfuel (or low-Btu) natural gas fields containing substantial amounts of helium have also been discovered. Because the gas from these reservoirs cannot be utilized as a fuel gas without first removing the noncombustible components of the mixture (a costly process) these exploratory wells have, for the most part, been cemented shut and abandoned. Finally, although exploration of the earth's crust for natural gases has resulted in the drilling of millions of exploratory and producing wells, practically all of these wells have been less than two kilometers deep. In certain areas, however, substantial gas deposits have been discovered at greater depths and it is possible that more natural gas (and probably more helium as well) will be discovered in the future as this next deeper layer of the lithosphere is explored. In other words, the helium resource story is still being written.

THE DEMAND FOR HELIUM

At present, at least three quarters of the world demand for helium is being satisfied by the United States. A decade ago, the fraction was even higher. Whether this US market share can be maintained in the future is far from certain and the reasons for this uncertainty will subsequently become apparent. For present purposes, however, it useful to examine briefly the history of helium production in the US.

The total market sales for US-produced grade A (>99.995%) helium from 1940 to 1984 is shown in Fig. 1. Although the commercial production of large amounts of

---

*One notable exception was the gas from the Pinta Dome field in Arizona. This natural gas consisted of about 8% helium with the remainder being essentially nitrogen. An extraction plant, built to process the gas from this field, produced a total of ~ 1×10^9 cf (~ $28 \times 10^6 m^3$) of pure helium from 1962 to 1976.

**The average helium concentration in the original natural fuel gas resource of the United States was about 0.1 vol.%, including the helium-rich resources in the southwestern region of the country. This concentration has now been reduced about 0.075 vol.% or less. Since natural fuel gas reserves and estimated resources in other parts of the world are substantially less rich in helium than are those of the US, it is believed that the 0.05 vol.% estimate is not unreasonable.

relatively inexpensive helium became possible soon after 1905 (since in that year large amounts of a rich and conveniently processed source material was discovered and a few years earlier the technology of cryogenic gas separation had been successfully demonstrated by Linde and by Claude), no attempts were made to produce large amounts of helium until 1915, no significant production of helium occurred until the spring of 1918 and, for the next twenty years, world production of helium (practically all of which was carried out by the Bureau of Mines of the US Department of the Interior) averaged only about 10^7cf/y($3x10^5m^3$/y). Furthermore, almost all of this helium was utilized in the US Navy's rigid lighter-than-air aircraft program during the 1920's and 1930's . Its tragic experiences remain as an example of a new technology which could not, at that time, be made sufficiently risk free to warrant pursuing - especially given the successes that were being achieved concurrently by the conventional aircraft industry. During this period one other practical use of helium was developed, namely that of a helium-oxygen mixture by US Navy divers and caisson-laborers to minimize adverse effects caused by the formation of gas bubbles in the blood upon decompression.[7] Neither of these applications resulted in any significant increase in the demand for helium, however, and hence, had the abscissa of Fig. 1 originated 20 years earlier, the total helium sales curve would have been almost indistinguishable from the time axis during practically all of that period.

In order to understand the data provided by Fig. 1, and, in particular, to comment rationally on the probable demand for helium in the immediate future, it is important to consider why this twenty to thirty year induction period preceeded the rapid growth in helium demand which began in 1940 and then continued more or less continuously for the past 45 years. One partial explanatio of this long induction period is the necessity, common to every developing nation, of focusing its initial effort upon the establishment of a heavy industry base. Given that base, it then becomes possible to move forward in the invention, development, utilization and continuous improvement of more sophisticated technologies (note that in this context all nations can be viewed as "developing"; they differ only in the extent to which they have progressed along the path of technological development). It can therefore be argued that a nation's advancement into the so-called "high technology" phase of industrialization becomes possible only when it has developed a sufficiently broad technological base, including, in addition to a heavy industry, an adequate number of well-trained scientists and engineers, the motivation to press forward in developing advanced technologies, adequate resources, capital, sophisticated instrumentation, diagnostic capabilities, etc. Finally, since new highly advanced technologies are particularly likely to require special materials with special or even unique properties and since helium certainly qualifies as such a material, the long delay in helium utilization by the industrialized nations of the world, and by the US in particular, becomes partially understandable.