Rare Gases

A FAST GROWING GLOBAL COMMODITY

By Richard Betzendahl

Williams Ramsay and Travers Morris discovered the three rare gases — krypton (Kr), xenon (Xe) and neon (Ne) — in 1889 when they found a remaining substance after distilling liquid air. These three gases are part of a family of gases, which also includes helium, argon and radon, known most commonly as the rare gases, but also are referred to as the "noble gases" or "zero-valence gases". Historically, these three gases have roots in the Greek language and were named clearly in reference to their rarity. The word krypton is derived from the Greek word Kryptos, meaning hidden, xenon means stranger, and neon is derived from the word neos, meaning new.

Interestingly, the rare gases are completely inert and chemically are extremely stable due to the fact that they all have an outer atomic ring that has the maximum number of valence electrons. Although these three gases, krypton, xenon and neon, represent only a minute fraction of air, their use in the industrial world is tremendous and growing. Illustrated in Figure 1 are some of the unique characteristics of these rare gases, which have allowed krypton, xenon and neon to become widely used in a variety of industries and applications.

THE PRODUCTION PROCESS

Rare gases are produced from specially designed large air separation plants (ASU) around the world. A small number of ASUs worldwide, about 75, are designed for rare gas extraction. Each of these plants, on average, can produce about 1,250,000 liters of gaseous Kr per year (125 cyl/year) and 110,000 liters of Xe per year (11 cyl/year).

RARE GAS PROPERTIES

Rare Gas	Chemical Symbol	Concentration of Air	Mol. Weight	Boiling Point (at 1 atm) Temp°F	Estimated WW Capacity (million ltr/yr)
Neon	Ne	18.18 ppm	20.2	-410.9	375
Krypton	Kr	1.14 ppm	83.8	-244	90
Xenon	Xe	.09 ppm	131.3	-162.6	10

Figure 1 Source: Betzendahl Gas Consultants

In the production process, Kr and Xe are produced together in the ASU column, which is equipped with distillation trays to concentrate the crude mixture. As the mixture contains hydrocarbon impurities and oxygen, it is passed into a separate crude column specifically designed to strip out most of the hydrocarbon impurities and oxygen, producing what is known as "crude rare gas." The crude is about 90 percent Kr and 7 – 8 percent Xe. Given the relatively small amounts of Kr and Xe in air, only very large ASUs are used to extract these gases. Depending on market pricing, it takes at least a 1,000-ton per day (tpd) plant to economically extract these gases. Once extracted, crude gas is filled into cylinders and transported to one of about 10 purification sites around the world. At these sites, a smaller cryogenic distillation column separates the Kr and Xe and purifies each to 99.999 percent. There are three facilities that extract Kr and Xe in the US today.

KR AND XE PRODUCTION

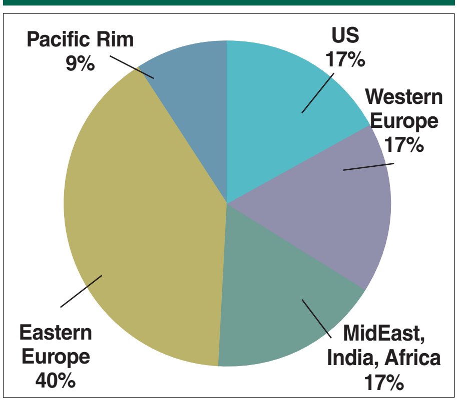

Figure 2 Source: Betzendahl Gas Consultants

The ratio of Kr to Xe in air is about 11 to 1, yet the world supply is 9 to 1. This difference is due to the fact that some ASUs built without internal concentration trays,were later fitted with extraction columns and can only extract about one-third of the Kr. These plants produce crude that is about 30 percent Xe with the balance Kr.

Neon, which has the third lowest boiling point after hydrogen and helium, is recovered separately in large ASUs using a special neon column to extract crude Ne. Once extracted, Ne is generally filled in tube trailers and shipped to one of about five purification locations around the world. There are only two such facilities operating in the US.

Unlike so many other industrial gases, rare gases are not based on local production, service, or capability, but are truly global commodities where the balance of demand, supply, and speculation, determine price.

WORLD PRODUCTION DATA

The current world production is just over nine million liters (.33 million SCF) of xenon, 82 million liters (2.9 million SCF) of krypton and around 375 million liters (14.4 million SCF) of neon. This production is controlled by the three largest industrial gas companies — Air Liquide, Praxair and Linde. There is also significant rare gas capacity in the former Soviet Union with one major purifier of crude, Iceblick, which controls most of that supply. Together, these four companies control more that 80 percent of all rare gases produced globally.

Crude Kr and Xe production has a high concentration of production in the former Soviet Union, which viewed rare gases as a strategic material for its space program after World War II. Under Soviet rule, many large ASUs were built to support the huge Soviet steel industry and were equipped with crude rare gas extraction and purification facilities.

Neon production is also spread around the world with over 70 percent produced in the former Soviet Union for the same reasons that Kr and Xe production were developed there.

PRICE FLUCTUATIONS

Market pricing for rare gases reflects the wide fluctuation in supply and demand from 1980. As new capacity takes years to bring on-line, pricing of rare gases is characterized by extreme swings when demand outstrips supply, or supply significantly exceeds demand.

Figure 3 shows rare gas price changes over the last 25 years and my projection for the next five years. (Figures are in current dollars and not adjusted for inflation.) During the 1980s, the major industrial gas companies controlled the production and sale of rare gases. Prices for Kr and Ne were fairly stable at that time, although prices for Xe spiked when xenon lamps began to be more popular. When the Soviet Union dissolved, previously produced gases in Russia's stockpile entered and flooded the world market and prices plunged in the early 1990s. This large supply at lower prices created only a modest increase in demand, with the market taking until the late '90s to absorb this excess supply. In addition, this huge increase in supply eliminated investment in new capacity in Europe, the US and Japan.

RARE GAS PRICE CHANGES

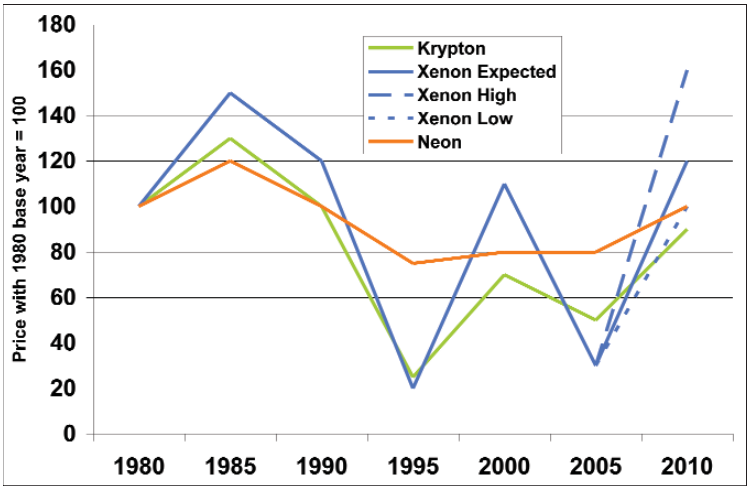

Figure 3 Source: Betzendahl Gas Consultants

In 1996, the market for low level telecommunications satellite market began to heat up. It was expected that 50 percent of the then current annual production of Xe would be used by satellites. At the same time, the market for Kr used in insulating windows was growing rapidly due to energy conservation schemes being introduced mostly in Europe. With the anticipated strong demand for Xe in satellites and Kr in windows and lighting, there was a sharp rise in demand, which led to additional crude rare gas recovery in new, very large, ASUs. But the satellite market never got off the ground (no pun intended) and satellite programs were scrapped, again leaving excess supply of Xe to be absorbed by the market. Prices for Xe decreased once more, as supply outstripped demand.

By 2005, the excess supply had been slowly consumed by new applications. Today there are rumors of new rare gas plants on the drawing boards. Prices had stabilized at a low during 2001 - 2005, then they began to rise in 2006. During the first quarter of 2007, we have seen the prices for Xe rise 50 percent, with Kr and Ne rising about 10 – 20 percent in the same quarter. By 2010, if just some of the new applications being developed materialize, supply will again be extremely tight. It is not inconceivable that prices could more than double from today's levels and be followed by a down cycle sometime after 2010. This is particularly true for Xe. Another possible scenario for Xe is, if its price rises too high in the short term, new applications as well as some older ones, will move to recycling and or other processes which do not use Xe. Either scenario creates the roller coaster effect seen in the price volatility of Figure 3. As you can see, the balance of supply and demand has been very hard to manage since 1980.

MAJOR RARE GAS APPLICATIONS

Lighting

Lighting is the number one application for the rare gases. The lighting industry uses a large portion of the Kr, Xe and Ne produced, in mixtures of each other and with argon.

Krypton, when energized as in a "neon" sign, glows greenish-orange. Kr is used in specialized lighting applications. Energized ionized Kr appears white, which makes it useful in any application needing bright white light. An additional benefit to Kr is its high molecular weight, which slows evaporation of the hot tungsten filament, leading to a longer-life light bulb. Kr is also used in florescent lamps mixed with argon, in spotlights and in many photographic lighting applications.

Xenon, when energized as in a "neon" sign, glows blue. Xe lighting has the ability to emit a very bright color approximating sunlight at noontime. Like Kr, xenon increases the life of the tungsten filament. Xe lighting is used in stadiums, automotive HID headlights, IMAX theaters, photography, and other concentrated bright-light applications.

Neon, when energized as in a "neon" sign, glows reddish-orange and is most familiar to us as a form of lighting for signs. It is also used in a few mixtures with either Kr or Xe for specialized applications.

The lighting industry is growing quickly as developing countries, such as China and India, expand their infrastructure. In addition to basic growth, the dramatic increase in fuel costs is causing a worldwide push to reduce consumption of energy, a major amount of which is used for lighting. This could increase the use of Kr, as many of the energy efficient long-life bulbs are Kr filled. At the same time the use of LEDs and compact fluorescents that use small amounts of Kr is growing. So I would expect some growth in Kr usage for the next few years, followed by a slow down, as LEDs and compact fluorescents improve in acceptance and cost and begin to replace those using Kr energy efficient long-life bulbs. For Xe and Ne in lighting applications, I see growth of 4 – 6 percent as Xe headlights and Ne in fluorescent lighting continues to grow at normal rates.

Laser Applications

Eximer and helium-neon lasers are the second major application for rare gases. Eximer lasers typically use an inert gas such as Kr, Xe or Ar, mixed with fluorine or chlorine. When these gases are "excited" with an electrical charge, they give rise to a monochromatic ray of light in the ultraviolet range. This light is well-focused and capable of very delicate control. It is absorbed efficiently and safely by biological matter and organic compounds, making it safe for medical procedures. Since eximer lasers give off very little heat, they are used for LASIK eye surgery and for micro-machining organic materials in the electronic industry. These applications have grown rapidly and continued growth is expected.

Helium-neon lasers are small lasers that use a mix of helium and neon in ratios of 5:1 to 20:1. They produce a red light and have been primarily used to drive bar code scanners. While many HeNe lasers have been replaced with diode lasers, they are still used in laboratories for optic demonstrations, in spectroscopy and for holography. These applications are fairly constant and do not represent a growth market.

KRYPTON-SPECIFIC APPLICATIONS

Insulated glass window manufacturing is a major consumer of Kr. This application uses as much as 40 – 50 percent of all Kr produced today. Air, argon and krypton are used in the production of double and triple-pain insulated windows. The use of rare gases as window insulators is growing as the cost of energy continues to climb and as the term "U value" is introduced into building codes. A "U value" is the amount of heat, in BTUs, that moves through a square foot of window in one hour, for every degree Fahrenheit difference in temperature across the window. The lower the "U" value the more efficient the window is as an insulator. Figure 5 shows the use of gases in windows and their associated "U" values.

In window insulation, Kr is most often used in a mix of Ar to keep costs down. Ar filled windows account for over 70 percent of all energy efficient gas-insulated windows manufactured today, with Kr and a few other gases making up the balance. A double-glass window filled with Kr in a 1/4 inch annular space will have twice the insulation factor as one with an air filled 1/2 inch annular space. We have seen the use of Kr windows grow rapidly in the colder regions of Europe over the last few years. Many European countries have requirements for low "U" value insulation and even require krypton in certain applications. The US, with its traditionally lower energy costs, has been slower to adopt lower insulation factors but today seems poised to change given currently record high energy costs. With the introduction of energy and insulation codes in Europe, we have seen the use of Kr increase dramatically in window insulation. This increase in demand, coupled with the demand for Kr generated by the lighting industry in developing countries, are the major causes for the demand increases from 2004 to 2010 shown in Figure 4.

KRYPTON SUPPLY AND DEMAND

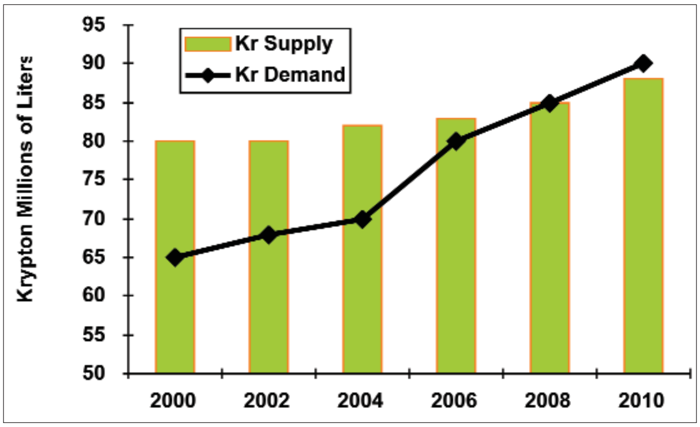

Figure 4 Source: Betzendahl Gas Consultants

"U" VALUE FOR GASES IN WINDOWS

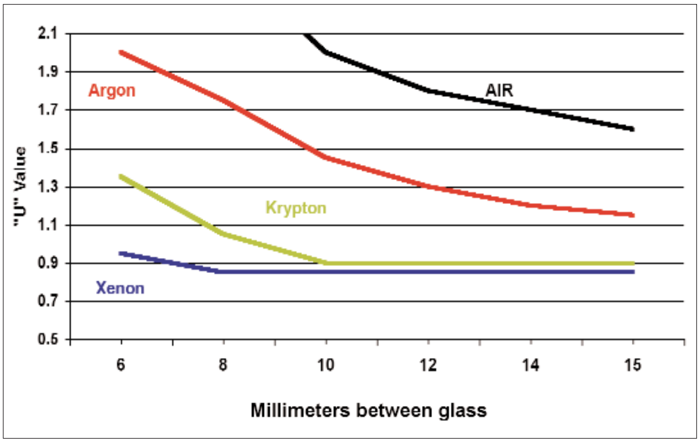

Figure 5 Source: J. Butkus , A. Vladisauskas, L. Jakevicius "The Use of Ultrasound for The Investigation of Glazing Units." Kaunas University of Technology.

XENON-SPECIFIC APPLICATIONS

The market for flat panel displays, specifically plasma TVs, has been a recent major contributor to the increase in Ne and Xe demand. Plasma display panels (PDP) are now being used for large TV displays (typically above 32"). A PDP is made up of many tiny cells located between two panels of glass that hold an inert mixture of Xe and Ne. The mix is from 5 - 25 percent Xe, with the balance as Ne. The gas in the cells is electrically turned into plasma, which then excites phosphors to emit light. LCD technologies, which are now less expensive and more common than plasma, may not be as effective in producing the quality of light at these new larger screen sizes. If plasma emerges as the winning screen of choice, its application could cause a significant increase in demand for both Ne and Xe. If LEDs become the consumers' first choice, it will reduce the demand of Xe. Pending the outcome of this question, demand could be five percent or 25 percent greater next year.

Ion engines and ion plasma thrusters for satellites are other applications for Xe. These two ion technologies are used for keeping satellites in orbit and use Xe because of its very heavy weight and density. A pair of grids in the ion engine, electrified with almost 1300 volts, accelerates the ionized Xe to very high speeds and shoots it out of the engine, providing thrust like a jet engine. In the ion engine, the Xe ions travel at about 35 kilometers/second (77,000 miles/hour). About 10 times faster than the exhaust from conventional rocket engines, Xe gives about 10 times as much thrust as chemical propellants. The Russians pioneered ion engine technology and created a large Xe production capacity as part of the Soviet Union military build up.

Satellite applications consume significant volumes of Xe for orbiting stability and maneuvering, with a typical satellite using as much as 60,000 liters. Communication satellite systems and unmanned exploration satellites run by Western governments are the major Xe consumers. Satellite applications have been fairly stable but with developing nations, particularly Russia, putting up their own communication satellites, this application is expected to grow rapidly over the next few years.

Medical applications for Xe provide new and promising growth areas with long-term potential. Xenon is used to enhance imaging in X-rays, CAT scans and most recently MRIs. An MRI alone cannot detect a great deal of detail in your lungs. With the inhalation of a xenon/oxygen mix, however, the MRI scan can pick up the necessary soft tissue detail to help doctors make more accurate diagnoses. Xenon has also been shown to be effective as a neuroprotectant that helps protect damaged nerve cells from dying in stroke and spinal cord injuries. Xenon, whose narcotic effect has been known for almost 60 years, has promise for use in anesthesia. Xenon has no interactions with other medications, has minimal effect on the circulatory system, and creates no hangover effect like other forms of anesthesia. When the patient stops breathing the Xe/O2 mix, he comes back to a normal state almost immediately making it an excellent

XENON SUPPLY AND DEMAND

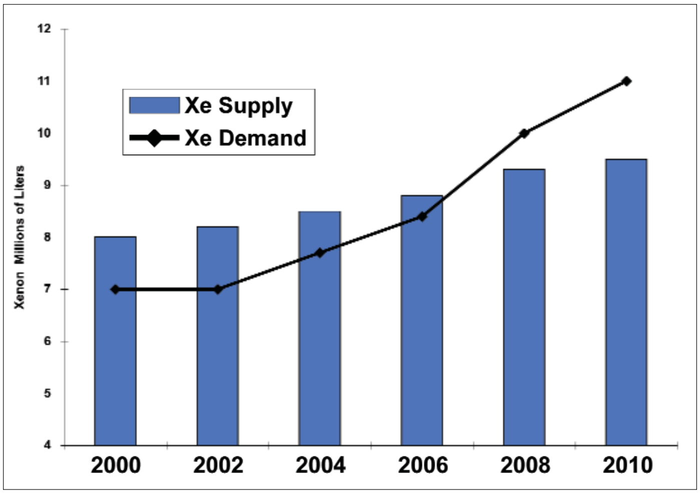

Figure 6 Source: Betzendahl Gas Consultants

NEON SUPPLY AND DEMAND

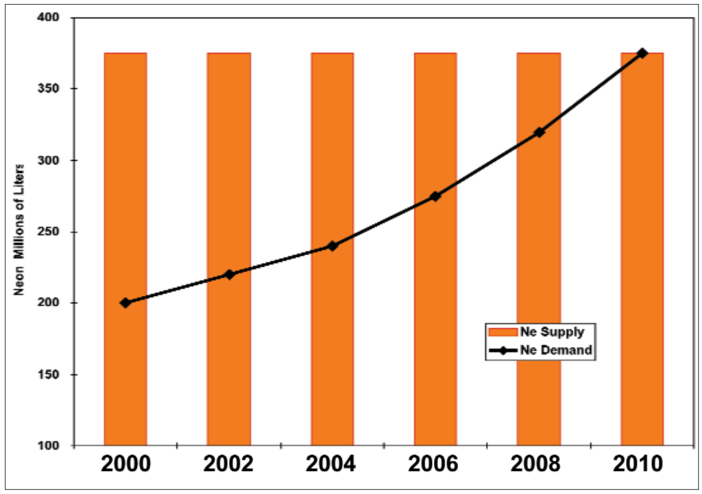

Figure 7 Source: Betzendahl Gas Consultants

anesthesia for high-risk patients, such as pregnant women, people with cardiac disease, and the elderly. A major drawback of Xe anesthesia is its expense. There are Xe recovery systems available to reduce cost. Without one, a one-hour operation would use as much as $5,000 of Xe. The world production of Xe could not currently support this potentially high demand. There are two Xe recovery systems available for Xe anesthesia procedures, one in Germany and one in Russia. In Russia, the consumption of Xe is expected to hit about five percent of the world production in 2008, from about 0.5 percent in 2004. The German use of Xe will increase to an estimated 10 percent of the world's production by 2011. If Xe use as an anesthetic were approved by the whole EU as well as the US, the demand for Xe would be 2 - 3 times the current world capacity.

The latest application for Xe is in electronic chip manufacturing, and is currently the most significant reason for Xe demand growth and speculation. A few major chip manufacturers are now using Xe plasma etching, primarily for the manufacture of "micro-electro-mechanical systems" or MEMS. These MEMS devices promise to combine microelectronics and micromachining technology, making possible more intricate and powerful circuits on a chip. Basically, this technology combines the computer chip (processing data) with sensors (gathering data) into one device, which can be mass-produced. Xenon etching is one process being used by some semiconductor manufacturers of this new breed of chip. The expected demand for Xe used in this application could be very large. It is estimated that this application will demand almost 30 percent of the world production in 2008. If this application uses the projected amounts of Xe, prices will double or triple and industry may move to recycling or a completely different alternate. Should this happen, we will see speculation push prices up, followed by a decline to more realistic price levels, as shown in Figure 3.

NEON-SPECIFIC APPLICATIONS

Neon applications are associated with other rare gas applications discussed previously. In Figure 7 you will note that the available production has remained the same for many years. This supply, as seen in Figure 3, has helped Ne maintain stable pricing for many years. Almost 70 percent of all Ne crude production is in Russia and the Ukraine. As the demand has increased, more crude is being recovered. In 2 - 4 years, supply and demand will meet and prices could rise rapidly.

CONCLUSION

The market variables are many in the products and processes that use rare gases. Over the next 12 - 24 months, several different scenarios could develop, but I believe that we were at a low price for all three gases, from 2000 through 2005. In 2007, we have already seen significant price increases for all these products. Demand is increasing rapidly, but supply only slightly. As described earlier, this slow increase in supply is due to the inability to financially justify adding rare gas capacity to an ASU while prices are low. With only three major gas companies and one eastern European purifier controlling more that 80 percent of world supplies, this could change quickly. As today's rare gas prices rise, producers can more easily justify new capacity. Unfortunately, getting new capacity on-line takes two to three years and must accompany new, large ASUs. Between now and then we are very likely to suffer through even higher prices for rare gases.

Neon, with its favorable supply capacity, will have the more modest price increases in the coming years. I estimate Ne price increases will be 5 – 10 percent per year. But if usage continues to grow we will see supply and demand meet in 2-4 years and this will put more pressure on pricing going forward. 2007 prices are already up about 10 percent on average and prices for smaller end-users are now above $.10 per liter.

Krypton, with rapid growth in the lighting markets of developing regions and the move to more energy efficient insulated window in colder regions, will see significant price increases. 2007 prices are already up 20 – 30 percent and I expect to see more increases over the next few years. The news for the small users is worse. Kr already in the $.40s per liter for this group and is expected to increase as much as 30 – 50 percent over the next few years.

Xenon, which is under the most demand/supply pressure, is the gas that will increase the most. Prices have already increased about 50 - 70 percent in the last 12 months. Assuming the applications grow as anticipated, I expect an increase of another 100 percent-plus in the next 12 months. Xenon for small users is already up to over $8.00 per liter. With the expectation of doubling in 6 - 12 months you could see small users at possibly $20/liter.

These increases may seem to be large but referring back to Figure 3, it is no more than a return to the prices of the late 1980s, and not even as high as mid-80s prices. Today rare gases appear to be an excellent opportunity for our industry, but if history repeats itself, we could again find the market over built and new applications not developing as expected. This would cause pricing to collapse as it did in 2000 – 2001. The supply and demand of rare gases is indeed, a tough balancing act.

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Tip of the Iceberg

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