IODINE

by Stanley T. Krukowski, Oklahoma Geological Survey

Two primary sources of iodine production are subsurface brines associated with oil and natural gas deposits, and as a byproduct from nitrate deposits in Chilean desert caliche. The largest source of iodine, however, is seawater, which contains 0.06 ppm, or about 31 Mt (34 million st). Seaweed of the family *Laminaria* can extract and accumulate from seawater up to 0.45 percent iodine on a dry weight basis.

Production

Chile has the largest iodine reserves, followed by Japan and the United States. They also are the largest producers of iodine, respectively. Chile produces iodine from iodate minerals as either co- or byproducts of nitrate production. Most iodine plants are located adjacent to nitrate plants. However,

some stand-alone installations are located where high concentrations of iodates occur in older nitrate tailings.

Japan and the United States produce iodine from sodium iodide solutions found in underground brines associated with petroleum and natural gas fields. Iodine also is produced from subterranean brines in Azerbaijan, Indonesia, Iran, Russia, Turkmenistan and Uzbekistan. China produces iodine as a coproduct in the extraction of sodium alginate from seaweed. The U.S. Geological Survey (USGS) estimated world production of iodine in 2015 to be 30.3 kt (33,936 s t), exclusive of U.S. production. The USGS last reported U.S. production at 1.57 kt (1,727 st) for 2005. U.S. producers have since withheld production information for proprietary reasons. Chilean iodine production was estimated to be 20 kt (22,000 st) for 2015 and reported Chilean iodine production in 2013 was 20 kt (22,000 st). Chile accounts for about 65 percent of world production (excluding U.S. production). Japan is the secondlargest producer of iodine. The USGS estimated Japanese production to be 9.5 kt (10,471 st) for 2015, compared with 9.5 kt (10,471 st) in 2014. Japan accounts for more than 31.3 percent of world production (excluding U.S. production). Companies in Chiba, Miyazaki and Niigata prefectures operated iodine production facilities. Chiba prefecture accounts for about 80 percent of Japanese production.

According to the USGS, the remaining 3.7 percent of estimated worldwide iodine production (exclusive of U.S. production) in descending order came from Turkmenistan, Azerbaijan and Indonesia. Production amounts for China and Russia were not available. Iran had completed building an iodine production facility with a capacity of 65,000 kt/a (71,600 stpy) in Golestan Province in 2008, but no production figures were ever released.

Operations

Panic purchasing of potassium iodide (KI) tablets as an anti-radiation measure after the March 2011 earthquake and tsunami in Japan and the Fukushima nuclear disaster caused supplies to tighten and prices to increase. In late 2013 and throughout 2014, however, iodine prices decreased, and then likely bottomed out in 2015. Overproduction, excess supply and increased competition in the marketplace during the period 2013-2015 forced producers to increase efficiencies and reduce costs at their plants. Depreciation of the Chilean peso against the U.S. dollar also contributed to Chilean producers' woes. Natural disasters in Chile accounted for damaged infrastructure upon which operations depended, although no or minimal damage occurred to production plants. Heavy rains in March (ironically, in the driest desert on Earth) and an earthquake in September were the major events.

Sociedad Quimica y Minera de Chile S.A. (SQM), the world's largest supplier, lost market share as a result of the above factors, and made steps to regain it. SQM committed spending \$180 million of its \$300 million capital expenditure plan of 2014-2015 in 2015. The investment is intended to increase product quality while reducing costs at its operations by increasing efficiencies. Increasing production capacity was not one of the goals. However, in September, SQM reported increased production at its Nueva Victoria plant. At the same time, it was announced that the mining operation at the Pedro de Valdivia facility would stop. SQM also set a goal of increasing its global market share from 26 percent to 30 percent without revealing any specifics.

Besides dealing with natural disasters, SQM faced

accusations from Chilean deputy Hugo Gutierrez, who represents the Tarapaca region of northern Chile in the lower house of the Chilean Congress, concerning possible aquifer depletion in the Atacama Desert by the company. Also, the Chilean economic development agency, Corporacion de Fomento de la Produccion (CORFU), claimed that SQM violated its lease agreement in its obligations in extracting lithium on CORFU land. Political scandal also plagued SQM when investigations probed allegations as to whether SQM money was forwarded to the coffers of the Independent Democratic Union to fund its candidates' election campaigns. In December, SQM reported that the U.S. law firm Shearman and Sterling LLP did not find any evidence that the company had bribed any public officials.

RB Energy Inc. announced in February that its wholly owned Atacama Minerals Chile (AMC) would continue at its normal course to produce between 1.1 and 1.2 kt (1,210 to 1,320 st) of iodine in 2015 at its Aquas Blancas plant. Under the companies' Creditors Arrangement Act (CCAA), RB Energy sought a financial and restructuring solution by initiating the sale of the iodine operation. In May, RB Energy released a statement that no firm offers had met the requirements of the sale and that receivership was imminent.

Campania de Salitre y Yodo de Chile (Cosayach Group or CG), the second largest producer of iodine in Chile, reported on its website that 2015 was the target date of the completion of its seawater pipeline. The 26-km (16-mile) steel and plastic piping is expected to pump 4 million cubic meters of seawater per year to its iodine plants over 1,100 m (3,600 ft) of altitude.

Russia's Tyumen Resources Co. (TRC) announced its intent to initiate new iodine/bromine production for the first time since the collapse of the Soviet Union. TRC plans to complete the construction of the facility by 2018, producing iodine at the Cherkashinskoye industrial site in Tyumen Oblast located in south-central Russia. The capacity of the operation, using a combined sorption-electrochemical method, is expected to be 1 kt/a (1,100 stpy). Most of Russia's current iodine production (180 t/a or 200 stpy) comes from the Troitsky iodine plant at Krasnodar Krai.

Domestic production

Four companies operating in the United States accounted for 100 percent of U.S. elemental iodine production. IOCHEM owns the largest U.S. iodine plant 1.2 km (0.7 miles) east of Vici, OK. Its annual production capacity is 1.2 kt (1,344 st). It is a subsidiary company of Toyota Tsusho America Inc. A long-term contract with Schering AG of Germany accounts for the majority of IOCHEM's production.

Woodward Iodine near the city of Woodward,

OK is owned by Ise Chemicals Corp. of Japan. The Woodward plant's annual production capacity is 800 t (880 st). MIC Specialty Chemicals (a subsidiary of Mitsubishi International) exclusively distributed the iodine produced by Woodward.

The iodine produced in Oklahoma from these two companies comes from brines in the Morrow Formation (Pennsylvanian). Brines contain iodine concentrations of about 300 ppm. Production wells penetrate the Morrowan trench at depths ranging from 1,525 to 4,000 m (5,000 to 13,000 ft). The plants receive the brines through a system of pipelines. Iodine is extracted from solution in a chemical process involving a series of oxidation and reduction reactions. The final product is elemental crystalline iodine of greater than 98 percent purity in the form of either flake or prill.

Iofina Inc. continues its exploration program on acreages known as the Atlantis and Triton projects in Montana. The Montana IO1 plant was shut down in 2015. Iofina's Montana water permit was under public notice, and, in a June 5 news release, the company stated that "the decision by the Hearing Examiner of the DNRC...was to deny the company's permit." Iofina petitioned for a review of the final order file with a hearing scheduled for Feb. 16, 2016. A decision is likely in the second quarter of 2016.

Iofina has five plants operating in Oklahoma. Production comes from an extraction process from third party oil brine streams located at brine water injection sites. The source of oilfield brines is natural gas wells in the Mississippi Lime play of southern Kansas and northern Oklahoma. The extraction technology provides mobility with small modular units and tolerates relatively high temperatures and hydrocarbon fouling. Iofina produced 569 t (637 st) of crystalline iodine in 2015 from its IOsorb plants in the United States. Despite reduced salt water disposal well water volumes by order of the Oklahoma Corporation Commission, earthquakes and weather events, Iofina plants produced a 73-percent increase in iodine over 2014 totals. In regard to future 2016 production, decreases in the amount of salt water disposal led Iofina to estimate a possible decline in output of between 10 percent and 20 percent.

Kiva Holding Inc. (KHI) is a new iodine producer located near Leedey, OK. Plans are to run trials at its blow-out process plant in July 2016 with production beginning in October. Projected output is 160 to 180 t/a (180 to 200 stpy).

Consumption

The USGS reported imports for consumption, crude content, of iodine in the United States increased from 5.36 kt (5,908 st) in 2014 to an estimated 6.3 kt (6,945 st) in 2015. Major uses in the United States include X-ray contrast media (XRCM), pharmaceuticals, liquid crystal display (LCD) screens and iodophors, in descending order. Other uses include sanitation, animal feed, catalysts, heat stabilizers, inks and colorants, photographic chemicals, laboratory reagents, production of batteries, highpurity metals, motor fuels and lubricants and others.

Major uses of iodine on a worldwide basis include X-ray contrast media, LCDs, polarizing film applications, iodophors, chemicals, organics, pharmaceuticals, human nutrition and animal feed, nylon production, and others. Iodophors are used in a variety of antiseptics, biocides and disinfectants in medical and agricultural applications. Iodine is used as an important catalyst in the production of various chemical intermediates.

Developing nations, such as China and India, represent potential markets for traditional uses of iodine. Veterinary antiseptics is one example for the Asia Pacific, Latin America and probably the rest of the world. New applications also offer potential new markets including the substitution of chlorofluorocarbons with relatively benign fluoroiodocarbons in refrigerants, in aerosols, in plastic foam blowing, in metal and electronics cleaning, and in fire suppression systems. The state of Maharashta in India proposed cloud seeding with silver iodide for drought relief.

Demand

The major growth drivers behind the increasing iodine demand though, are its use in X-ray contrast media LCD applications and light-emitting diodes (LEDs, two-lead semiconductor light sources). The increased use of iodine in LCDs is due to the demand for television and computer screens — particularly the growing demand in quantity and size for large screen televisions. Increased usage of LED lighting is responsible for the demand in this sector. The majority of applications are related to human and animal health and nutrition. Additional main applications include biocides, disinfectants, iodized salt and synthetic fabric treatments (nylon).

Major demand for iodine is for use in blocking the uptake of radioactive iodine isotopes responsible for thyroid cancer. Potassium iodide (KI) prevents such cancers and, is therefore a staple for residents proximal to nuclear power plants. Panic purchasing immediately after the Fukushima nuclear power plant disaster in 2012 caused iodine prices to increase steeply.

The demand for iodine also increased in several traditional applications including as a catalyst in the chemicals industry, particularly in acetic acid production. Acetic acid is used as a solvent in terephthalic acid which is used in the production of soft drink containers. The largest market for acetic acid is in the production of vinyl acetate.

Increased demand for iodine as a disinfectant and

Industrial Minerals

in water treatment continued to increase as developing nations expanded treatment of water supplies.

Prices

The price for iodine at the beginning of 2015 was US\$31 to \$37 (iodine crystal, 99.5 percent min, drum, per kilo; contract) and US\$31 to US\$35 (iodine crystal, 99.5 percent min, drum, per kilo, spot), as reported by *Industrial Minerals*. In January 2016, *Industrial Minerals* reported prices for iodine (crystal, 99.5 percent min, drums) at US\$27.50 to US\$32 (crystal, 99.5 percent min, per kilo) on a spot and contract basis. Speculation is that this may be close to bottoming out.

Although increased demand for X-ray contrast media, LCD polarizing films, LEDs, agricultural

intermediates (agrochemicals) and human and animal nutrition remained high prices were especially affected when panic purchasing of KI tablets subsided as recovery from the March 2011 tsunami in Japan occurred, competition increased among producers and oversupply became a factor. The continued demand for iodine should increase at a more moderate 3 percent pace in 2016.

Substitutes

Bromine and chlorine could substitute for iodine in biocides, colorants and inks. But in most categories, they are considered inadequate. Iodine cannot be replaced in some pharmaceuticals, catalytic uses, and human and animal nutrition. Antibiotics and boron also may substitute for iodine as biocides.