MASTER

**A Survey of the Market,
Supply and Availability of Gallium**

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ABSTRACT

The objective of this study was to assess the present consumption and supply of gallium, its potential availability in the satellite power system (SPS) implementation time frame, and commercial and new processing methods for increasing the production of gallium.

This study resulted in the following findings:

1. There is presently an oversupply of gallium in the free-enterprise world (estimated 25 metric tons production capacity vs. 14 metric tons consumption in 1978).
2. The primary sources of gallium are bauxitic ores containing 0.003-0.009% gallium; they account for over 90% of the world supply of gallium.
3. Commercial processes for extracting gallium from bauxite are 30-50% efficient; but the potential exists for extraction efficiencies as high as 80%, if an accelerated demand warrants such process modifications.
4. Less than 2% of the bauxite used for obtaining alumina in primary aluminum production is processed for gallium extraction.
5. Data on the primary aluminum production from bauxite throughout the free-enterprise world suggest that approximately 1,370 metric tons of gallium were potentially available in 1978 using conventional extraction technologies.
6. Approximately 65% of the world bauxite comes from Australia, Guinea, Jamaica and Surinam. The first three also have large commercially proven reserves. With its new discoveries of bauxite ores, Brazil may also become a major producer within the next five years.
7. The United States, which is the major producer of primary aluminum, relies heavily on foreign sources of bauxite principally from Jamaica, Surinam, Guyana, the Dominican Republic, Haiti and Guinea.
8. The world-wide commercial reserves of bauxite total 27 billion long tons, a 320 year supply at the 1978 production level of 84 million tons. Estimated cumulative demand for bauxite by the year 2000 is still only 13% of current commercial reserves.

The above findings strongly suggest that with proper long range planning adequate gallium would be available from free-enterprise world supplies of bauxite for SPS implementation.

1. INTRODUCTION

A primary responsibility of NASA as part of the Satellite Power System (SPS) Concept Development and Evaluation Program (CDEP) was to define a SPS reference system. This was accomplished and documented in the October 1978 Reference System Report.¹ The satellite for the reference system was photovoltaic, with single crystal silicon (Si) and gallium aluminum arsenide (GaAlAs), as materials options for the solar cells. The GaAlAs cells have many advantages; higher efficiency leading to lighter weight, higher operating temperature, radiation damage resistance and passive annealing of radiation damage. They are more expensive (double the cost of Si) but their lighter weight for a given power output results in offsetting reduction in transportation costs.

The Department of Energy (DOE) evaluation of the SPS has shown a serious shortfall of gallium required for a fully implemented SPS program. The 5 GW SPS using GaAlAs solar cells would require 390 metric tons of gallium. At the projected production rate of 10 GW per year, this represents a 3,200% increase over present, free-enterprise world production capability (25 metric tons) and 56% of the potentially available gallium (1,370 metric tons) from bauxitic ores currently processed to produce primary aluminum. A network of such satellites would necessitate an essentially new gallium recovery industry which, for economic reasons, would have to be coupled closely with the aluminum industry. The specific objective of this study was to determine the potential availability of gallium for the SPS and to denote how the recovery could be implemented.

2 APPROACH

Under Order No. H-34356B and Requisition No. 1-8-PP-00834(1F), a study was authorized by NASA, Marshall Space Flight Center (MSFC) to survey the present and potential availability of gallium metal in connection with materials evaluation recommendations for satellite power systems. This evaluation focused on the following areas:

- O Market considerations - the present and emerging uses of gallium, as well as the consumption and price of gallium.
- O Supply considerations - present sources of gallium, commercial and new methods for extracting gallium from bauxite, and summary comments.
- O Methods for purifying gallium to satisfy market demands.
- O Principal suppliers of gallium.
- O Gallium availability from bauxite on the basis of primary aluminum production, and bauxite production, reserves and resources.

The study was based on published information as well as information derived from private communications with both major and potential suppliers and users of gallium and with staff members at the Bureau of Mines.

3 DISCUSSION

3.1 MARKET CONSIDERATIONS

3.1.1. Present Uses of Gallium

The major market for gallium is the electronics industry, which requires gallium in its highest purity form (99.9999%). This is clearly indicated by the data in Table I, which shows gallium consumption by end use in the United States for the years, 1975-77.

Table I. U.S. Consumption of Gallium by End Use in Kilograms*

End Use	1975	1976	1977
Specialty Alloys	7	4	4
Electronic Devices	7,338	8,210	7,965
Research and Development	91	609	763
Unspecified Uses	57	57	57
Total	7,493	8,880	8,709

*Bureau of Mines Minerals Yearbook, 1976 and 1977

The electronics market comprises the use of the compound semiconductors, gallium arsenide (GaAs) and gallium phosphide (GaP), solid solution alloys of these compounds, and alloys of gallium arsenide with aluminum arsenide (GaAs-AlAs) in a variety of electronic devices. These include:

- O Light-emitting diodes as indicators and numeric displays for use in calculators, telephones and digital watches - and as infrared illuminators for night vision, vision through fog and smoke, ranging devices, and communication links.
- O Amplifiers and oscillators for high frequency microwave communication systems (4-30 gigahertz bandwidth), as well as microwave devices for radar, navigation, and intrusion alarms.

- O Photocathodes and secondary electron emitters in photomultiplier tubes for use as sensitive light detectors in scintillation counters and spectrometers and for direct imaging applications.

Much smaller amounts of gallium are used in such diverse applications as dental alloys, manufacture of optical mirrors, radioactive compounds, low resistance contact electrodes, spectrographic analysis of uranium, fuses in signalling devices, and as a sealant for glass joints.

3.1.2 Emerging Uses of Gallium

Table I shows that a significant amount of gallium is used for research and development purposes. This effort is largely related to the development of a broad variety of electronic devices, which have a high probability for commercialization. These potential uses of gallium, which can significantly expand its market, include the following:

- O Magnetic "bubble" memories, which require a gallium oxide-gadolinium oxide substrate for synthesizing single crystal films of the unique magnetic materials (mixed rare earth iron garnets) responsible for the functions of information storage and manipulation.
- O Infrared laser diodes of gallium arsenide for communicating telephone messages transmitted through trunk cables of optical fibers.
- O Photovoltaic devices using gallium arsenide for the efficient and reliable conversion of solar energy directly into electricity for both space and terrestrial applications.
- O High-field superconducting magnets using the compound, niobium-gallium (Nb_3Ga) for the economic generation of electricity by fusion and magneto-hydrodynamic power systems, and for use in electric power generators and motors with large increases in power per unit volume and efficiency.

Telephone communication systems using laser-based fiber optics have been undergoing commercial trials by the Bell Telephone System in Chicago, Illinois and Atlanta, Georgia with reports of considerable success. In fact, the Bell System has recently announced plans to build a \$79 million fiber optic telecommunication system from Washington, DC to Cambridge, Massachusetts (over 600 miles) capable of carrying 80,000 conversations along gallium arsenide laser-produced light waves.

Magnetic "bubble" memory prototypes have been developed with storage capacities, speeds of information handling, and a reliability which could make them economically competitive with their semiconductor and magnetic counterparts for certain applications. Bubble memories are expected to replace first the conventional magnetic disc systems for data storage - a trend which will gain momentum as relative systems costs continue to favor bubbles. In 1978, Texas Instruments announced a 256 K-bit bubble memory, which is the highest complexity component yet developed and whose performance suggests accelerated use in memory systems.

Gallium arsenide solar cells have been developed with efficiencies of 20-22%, which is somewhat higher than that achieved with any other semiconductor material. The superior high-temperature characteristics of these cells also makes it possible to increase their efficiency by the use of concentrated sunlight; and in fact, cell efficiencies of 24.6% have been demonstrated with a 180 x concentration of sunlight. The performance of GaAs cells has further been shown to be less affected by energetic electron and proton radiation - an important consideration for space applications. The chief disadvantages to the widespread use of GaAs as a competitive material in solar cells are materials and cell fabrication costs, which must be significantly reduced. This will require many man-years of intensive research and development.

The feasibility of the basic concepts for superconducting electric power generators has been amply demonstrated by an 80KVA machine at M. I. T., and by construction of a 1 MVA generator at Westinghouse. Design plans are also underway at M.I.T. for a 1,000 MVA machine, which is comparable to conventional generators used by utility companies.

In addition to the above devices and products, gallium in the form of gallium chloride is also used for measuring neutrinos emitted by solar radiation. This experimental work, which is presently being done at the Brookhaven National Laboratories, can lead to a significant demand for gallium. Brookhaven estimates that 50 tons of the element per year would be required if widespread use were made of this neutrino measurement technique.

3.1.3 Consumption and Price of Gallium

Definitive data on the current, free-enterprise world consumption of gallium are not available. However, gross estimates from a variety of sources indicate a range of 12,000-14,000 kg. per year. Major consumers are the United States, Japan, West Germany and England, since these countries are active in the manufacture of electronic devices using gallium compounds and have developed significant markets for these devices.

The domestic consumption of gallium for the years 1973-77 is given in Table II, taken from the Bureau of Mines Minerals Yearbook, 1976 and 1977. The 1978 data are projected estimates. Also included in Table II are imports of gallium to meet domestic demand, and the average price of the high purity form of gallium required

Table II. Salient Gallium Statistics in the United States

	1973	1974	1975	1976	1977	1978*
Consumption (kg.)	8,496	6,939	7,493	8,880	8,789	8,500
Imports (kg.)**	11,124	6,536	6,830	4,920	2,884	2,400
Av. Price (per kg.)	\$750	\$750	\$775	\$550	\$550	\$550

* Projected estimates

** Gallium metal only

for electronic devices. Several features are worth noting from the data:

- O The sharp drop in consumption in 1974 can be attributed to a severe economic recession, which was associated with unusually high business inventories of electronic devices.
- O The level of imports to balance demand has been decreasing markedly in the past three years, signalling increased reliance on domestic production of gallium. The 2,884 kilograms of imports in 1977 came from Switzerland (1,485 kg.), West Germany (774 kg.), Italy (349 kg.) and Canada (276 kg.).
- O The consumption of gallium has been relatively constant over the indicated five year period at approximately 8,800 kilograms, if one discounts the impact of the 1974 recession and the gradual economic recovery during 1975. This is to be contrasted to the rapid rise in consumption from the late 1960's to the early 1970's.
- O The average price for a kilogram of 99.9999% gallium has decreased significantly in the past two years from \$775 to \$550, reflecting possibly an over-supply situation most likely due to excess capacity and over-balanced inventories of foreign producers. At \$550 per kilogram, the domestic gallium market in 1977 was \$4,834,000.

- O There was a large imbalance of imports in 1973 compared with actual consumption, which was probably due to a building of gallium inventories in anticipation of a continued rapid increase in the demand for gallium by the electronics industry. This did not materialize because of the recession which immediately followed, and probably because the forecasted market growth was overly optimistic.

It is very likely that the present electronic markets using gallium devices have only moderate growth potential. If so, then the annual consumption of gallium cannot be expected to increase at a significant rate over the next few years; and the present world production capacity, estimated at 20,000-25,000 kg., would be more than adequate to satisfy foreseeable demand. Of course, this situation can change significantly if the above mentioned new electronic applications become commercial and, in particular, the magnetic bubble memories and gallium arsenide solar cells. The motivation for this, as well as the broadening of existing markets for gallium, would be greatly enhanced by a continued decline in the price of 99.9999% gallium. Presently, this appears to be the trend, since the average price per kilogram is now down to \$525 according to the May 9, 1979 issue of American Metal Market. On the other hand this trend may be reversed, since new facilities constructed with 1980 dollars coupled with increasing interest charges can only result in raising the market price for gallium. It is presently difficult to estimate the minimum price for gallium, which can be economically produced in a market requiring much higher volumes of the metal. The highly proprietary aspects of gallium extraction technology prohibit this.

3.2 SUPPLY CONSIDERATIONS

3.2.1 Sources of Gallium

Gallium was detected and isolated in 1875 by the French chemist, Lecoq de Boisboudran. According to geochemists, the earth's crust contains on the average 10 grams per ton of gallium, which is similar to the concentration of lead and arsenic. Unfortunately, it is widely distributed, and most of the gallium-bearing minerals contain significantly less than 0.5% of the metal. The richest gallium ore is germanite (Ge,Cu,Fe sulfide) which contains 0.5 to 1 percent of gallium and is found in South Africa. It is a rare mineral and not available in commercial quantities. Hence it cannot be considered an important source for gallium.

A number of zinc ores, such as sphalerite (ZnS), as well as certain copper and lead ores, have been found to contain as much as 0.001 to 0.05 percent gallium, which can be concentrated during the extraction processes for the zinc, copper and lead. Similar concentrations of gallium are also found in many coals, including coal and lignite ash. This level of gallium concentration and the availability of these ores and residues has generated considerable interest among potential suppliers. However, the high material, labor and processing costs associated with the gallium extraction makes these sources economically unattractive under present market conditions.

The most important commercial sources of gallium are presently the bauxite ores from which aluminum oxide (alumina) is refined and then electrolytically converted to primary aluminum. The data in Table III show that these ores, which are found in many regions of the world, contain only 0.003 to 0.009 percent gallium. However, this concentration can be increased by orders of magnitude through chemical processing of the sodium aluminate liquor obtained from alumina production by the Bayer process. The gallium can then be recovered economically by precipitation and electrolysis techniques, and as a by-product of aluminum ore extraction. The enormous volume of bauxite, currently processed throughout the world primarily for alumina production, could represent a potential source of large quantities of gallium.

3.2.2 Commercial Methods of Gallium Extraction

This section will deal solely with commercial methods of extracting gallium from bauxite or, more specifically, from the sodium aluminate liquor of the Bayer process for alumina recovery, since this represents the bulk of the world supply of gallium.

The processes for gallium extraction from this Bayer liquor fall into three general categories:

- (1) Recovery of a gallium concentrate from the sodium aluminate solution, and then the recovery of metallic gallium from the concentrate by conventional electrolysis.
- (2) Direct electrolysis of the sodium aluminate solution with a mercury cathode to form a gallium amalgam, followed by conversion to a sodium gallate solution yielding gallium metal on electrolysis.
- (3) Production of sodium amalgam from solution using a mercury cathode, and extraction of gallium by reaction of sodium amalgam with the gallium in solution.

The first method is used primarily by those companies who employ the lime-sinter process for alumina recovery, such as Alcoa. The second method is used by companies, such as Alusuisse, who rely on the Bayer process. The third method, as well as the second, are believed to be favored by many of the Eastern European countries.

Table III. World Sources of Bauxite and Average Gallium Content in Bauxite

<u>Country</u>	<u>Gallium Content (%)</u>
Australia	0.007
Brazil	0.005
Cameroon	0.004
China	0.006
Costa Rica	0.003
France	0.008
Ghana	0.008
Greece	0.004
Guinea	0.006
Guyana	0.005
Haiti	0.006
Hungary	0.004
India	0.006
Indonesia	0.005
Italy	0.005
Jamaica	0.006
Japan	0.005
Malaysia	0.004
Sierra Leone	0.003
Surinam	0.009
U.S.S.R.	0.005
United States (Arkansas)	0.008
Yugoslavia	0.005

Sources: Gallium Bulletin Information, No. 12 (1973-1974); published by Alusuisse-France S.A.
U. S. Bureau of Mines (1975)
I. Valetton; Developments in Soil Sciences I: Bauxites, Elsevier Publishing Co. (1972).

a. Gallium Concentrate Processes

There are essentially two processes in connection with the first method of gallium extraction, which are used to increase the gallium concentration in solution to permit recovery of metallic gallium by electrolysis. These are: carbonation and lime-alkali.

The carbonation of the Beja process² (patent assigned to Pechiney) was first introduced in 1936 but did not come into commercial use until after World War II. This process utilizes the fact that gallium oxide (Ga_2O_3) is slightly more acid than aluminum oxide (Al_2O_3). It consists of treating the aluminate solution with carbon dioxide in several carefully controlled stages, such that most of the alumina (about 90%) is precipitated first leaving the resulting liquor enriched in gallium. From this an alumina rich in gallium is obtained (about 1%). This is dissolved in caustic soda, and fractional carbonization is repeated until the mixed oxide is sufficiently enriched in gallium to permit recovery of gallium from the caustic soda solution by electrolytic deposition.

The lime-alkali or Frary process³ (patent assigned to Alcoa) was responsible for the first commercial production of gallium by the aluminum industry in the United States. This process increased the concentration ratio of gallium to alumina by first treating the aluminate solution with hydrated lime to precipitate the greater part of the alumina as calcium aluminate. Since calcium gallate does not precipitate as rapidly as the calcium aluminate, a considerable increase (by a factor of 15 or more) in the gallium to alumina ratio in the liquor is obtained. The liquor is then rapidly gassed with carbon dioxide, as in the Beja process, to co-precipitate the alumina and gallium. After suitable heat treatment, this precipitate contains 1.3% Ga_2O_3 , or a gallium to alumina ratio of 0.03. This solid is dissolved in caustic soda solution, from which the gallium is recovered by conventional electrolysis.

b. Direct Electrolysis with Mercury Cathode

The second method of gallium extraction, the mercury cathode electrolysis, is the de la Bretque process⁴ assigned to Alusuisse, in 1955. Here, the Bayer aluminate liquor is directly electrolyzed using a highly agitated mercury cathode. The cathode agitation is essential, because without it there is no gallium deposit. The agitation enables the gallium to form immediately a dilute amalgam at the surface characterized by a low gallium concentration and activity. The net result is that the rate of deposition of the gallium at the cathode far exceeds the rate of its solution. In addition, vanadium poisoning of the cathode surface is avoided through the reduction of pentavalent vanadium in solution. When a concentration of 1% gallium is obtained in the amalgam at the cathode, the mercury is drawn off and treated with a caustic soda solution. This provides a concentrated solution of sodium gallate, from which direct electrolysis gives gallium metal.

A modification of the de la Bretque process (the third gallium extraction method) was introduced in 1959 by Bielfeldt and Laspeyres⁵ (German patent assigned to V. A. W.) for the main purpose of minimizing losses of mercury resulting from a fine dispersion in the liquor caused by the vigorous mechanical agitation of the cathode. This process variation involves the preparation of a sodium amalgam by electrolysis with a mercury cathode of the circulating aluminate liquor or from caustic soda solution. Extraction of the gallium occurs by a cementation process whereby the action of the more electropositive sodium in the mercury amalgam displaces the gallium in solution. Subsequent recovery of gallium metal from the mercury follows the same steps as in the de la Bretque process.

3.2.3 New Extraction Methods

a. Reynolds Metals

A patent assigned to Reynolds Metals Company in 1975 describes a new process⁶ for enhancing the concentration of gallium in caustic solutions containing gallium

and aluminum (e.g., the Bayer liquor), and then recovering the gallium metal by conventional electrolytic techniques. The process involves the addition to the sodium aluminate solution of silica, which selectively reacts with alumina between 212°F - 400°F alumina to form an aluminosilicate precipitate leaving a solution enriched in gallium. The solution is then fed to an electrolytic cell for recovery of gallium metal. The advantages cited for this novel process over prior art techniques is that (1) it provides liquor to the electrolytic cell with higher concentrations of gallium, and (2) the process of gallium concentration is simpler and less expensive. The process actually appears to be more complex than the commercial ones, and is less adaptable to a normal Bayer circuit operation than even the Frary process. It has not been commercialized. Reynolds has also carried out pilot plant studies⁷ using anhydrous Dawsonite (a sodium aluminum carbonate) from the Bayer process which is dissolved in a NaOH solution to make a gallium containing electrolyte for electrolysis using nickel electrodes.

b. British Aluminium

The British Aluminium Company, Ltd. has done considerable research and development on a new metal cathode process⁸ for recovery of gallium from the Bayer liquor. The process starts with a strong Bayer liquor, which is diluted, heated to 50°C, and then electrolysed using preferably a tin foil cathode and nickel anodes. The tin-gallium alloy at the cathode consists of approximately 2.7% gallium, which is recovered by alkali fusion and then electrolysis in a dilute solution of sodium hydroxide. Depending on the method used for liquor purification (storage only to settle impurities or a combination with forced settling by centrifuging), the expected efficiency of this process for gallium recovery is 40-45%. It is claimed that the cost of producing gallium metal by this process will be no greater than the mercury cathode, sodium amalgam and the Frary lime-alkali processes. Moreover, the process is expected to offer the following advantages: (1) it should be simpler to obtain 99.9999% gallium, since tin is the only major contaminant at 0.02 - 1.6% levels; (2) it is operationally safer and less polluting than the mercury cathode process; and (3) it is more readily integrated with the Bayer circuit (as are all electrolytic methods) than the Frary process. The tin cathode process has not yet been commercialized. Other cathode metals under investigation are lead, indium, zinc and tin-lead alloys.

c. SNP - Czechoslovakia

The SNP enterprise in Czechoslovakia was awarded a patent in 1972 for a gallium production process⁹, which is claimed to have been in commercial operation since 1969. Actually it is not a chemically or electrolytically novel process. However, the chief advantages cited are flexibility and simplicity of process equipment for purposes of a continuous operational cycle for producing not only alumina but concurrently high purity gallium. It is adaptable to both the concentration of gallium in solution by the Béja process of carbonization, and the Bayer process using cementation. For both processes, extraction of gallium metal is accomplished by production of a sodium amalgam and electrolysis using a mercury cathode. High purity gallium is obtained by a continuous operation involving a second electrolysis, crystallization, zone refining and vacuum refining. Other advantages cited are high gallium production and energy efficiencies due to a new cementation design, which also results in a decrease in the mercury consumption by a factor of ten.

d. Russian Process

A recent Russian process¹⁰, which claims a process efficiency of 80% for gallium recovery directly from the sodium aluminate liquor with a 99.9% purity, was recently (1977) advertised for license in the book, Soviet Technology and Engineering Digest. The impurities in the gallium are mainly copper (0.004%) and lead (0.003%), which make it readily possible to achieve 99.9999% purity. The key elements in the Russian process, which is covered in two U. S. Patents¹¹, are the removal of vanadium pentoxide (V₂O₅) prior to electrolysis in the purification process, and the electrochemical displacement of gallate ions by aluminum from a liquid Ga-0.2 to 6.0% Al alloy. This is accomplished by stirring the alloy into the sodium aluminate solution containing

gallium oxide, whereby the aluminum in the alloy is replaced either batch-wise or continuously using the electrical potential of the alloy as a means of control. The process eliminates the mercury cathode and dispenses with carbonization. The Russian process for the electrochemical displacement of gallate ions by aluminum from a Ga-Al alloy is not considered a defensible patent, since related processes appear in two Johnson, Matthey and Company paper patents¹². However, the combination of liquors, alloy composition, mode of stirring, and process control may be technologically unique. There is no evidence that the Russian process has been adopted commercially. The materials flow diagram for this new process is shown in Figure 1.

Fig. 1 - Schematic diagram of the Russian process for recovery of gallium

3.2.4 General Comments on Commercial Extraction Processes

There is very little information on the materials costs, capital costs, and actual operational performance of existing gallium recovery plants for a meaningful comparison. The Béja process of treating the aluminate solution with carbon dioxide (carbonization) and electrolytic recovery of gallium from the caustic soda solution is probably no longer in commercial use. Pechiney, who holds the patent on this process, is known to be working on the mercury cathode electrolysis process.

The Frary lime-alkali, wet chemical process is considered more complex on the basis of equipment requirements for its operation, which could result in high capital costs. It involves several batch operations requiring two reaction vessels, two filtrations and a calcination stage, which suggest high labor costs. Most important, it cannot readily be incorporated into the Bayer circuit, since the processed sodium aluminate solution is not returned directly to the circuit.

As already indicated, the de la Breteque mercury cathode electrolysis process has the problem of a high mercury loss due to its fine dispersion in the Bayer liquid as a result of the essential need for cathode agitation. There is also the associated pollution problem. The sodium amalgam cementation process, as a modified version of the direct mercury cathode method, would appear to reduce the mercury losses. However, this entails additional process steps, and precautions must still be taken to avoid mercury losses into the Bayer circuit. It is claimed, nevertheless, that the capital cost is 50% lower than the de la Breteque direct mercury process due to lower space requirements, lower mercury inventory, and higher current efficiencies. In addition, the production costs are estimated to be significantly lower.

There is no definitive data on the operational efficiency of gallium recovery by these four processes, nor on current efficiencies. Present estimates of gallium recovery range from 30 to 50 percent. However, Alcoa and the Russians have indicated that 80% efficiencies are possible, but fail to specify methodologies for accomplishing this high value. At any rate, it would be desirable for an independent source to conduct research and development on the comparative materials and current efficiencies of at least the Frary, de la Breteque and sodium amalgam processes. Such information would go a long way towards providing realistic data on materials, process, and energy costs - and hopefully on a fair market price of gallium which can be economically recovered irrespective of supply and demand conditions.

By way of summary, Fig. 2 shows a schematic diagram of gross process steps commercially used for extracting 97-99.9% gallium from bauxite.

Fig. 2 - Schematic process steps in commercial methods for extracting gallium from bauxite

3.3 OTHER CONSIDERATIONS

3.3.1 Purification Methods

The purity of gallium produced by commercial processes in its separation from the Bayer liquor generally ranges between 97-99.9%. The impurities commonly present in this form of gallium are Zn (up to several percent), Pb and Fe (0.1% or less), and much smaller amounts of Al, Cu, Hg, Mg, Mo, Si, Sn and Ti. Many of these occur in the surface oxide or as a fine dispersion, and their removal can be accomplished by filtration of the liquid metal, and by heating under vacuum. By employing an acid-alkaline treatment involving sequential washing with hydrochloric acid, or by electrolytic refining involving anodic dissolution of gallium in an alkaline solution and then deposition at a liquid gallium cathode, these metallic impurities can be further reduced to less than 0.01%. Thus, techniques have been well developed for achieving a gallium purity of 99.99%.

There are several additional purification methods for obtaining a purity of at least 99.9999% (or 6 nines) required for electronic device applications. One method involves the conversion of gallium to a halide compound, such as GaCl_3 , which is then zone-refined. The high purity gallium is recovered from the trichloride by electrolysis. Another technique, known to be used by Alusuisse, is the gradual crystallization of molten gallium by the Czochralski or Bridgman technique in the form of essentially single crystals. High purity has also been achieved by heating fine droplets of gallium at high temperatures in a nitrogen or ammonia atmosphere. Here, nitrides of the impurities are formed at the surface, and then removed by flow of the molten metal through a capillary. Other high purity purification methods include the decomposition of trialkyl gallium compounds, formation of amalgams at elevated temperatures, and the disproportionation of dihalide compounds.

With the achievement of high purity gallium is the accompanying problem of analyzing definitively for the remaining impurities. The most reliable methods is optical spectroscopy and mass spectrometry, but electrical resistivity measurements at low temperatures are also commonly used.

Needless to say, the price of gallium increases markedly with higher degrees of purity (\$100 per kilogram more in going from 99.99% to 99.9999%).

3.3.2 Suppliers

According to Table II, the U. S. consumption of gallium in 1977 was approximately 8,800 kg. On the reasonable assumption that Western Europe and Japan consumed an additional 5,000 kg. in view of their extensive activity in electronic devices, then the Western World consumption of gallium is presently estimated to be about 14,000 kg. or 14 metric tons per year. Over 90% of this supply comes from bauxitic sources, and the remainder from zinc production residues and recycling efforts. Since the estimated free enterprise world production capacity is about 25 metric tons per year (11 tons from the United States and 14 tons from Western Europe), it is apparent that a potential over-supply situation exists. Consequently, future capacity expansion cannot be expected, unless new uses for gallium increase dramatically.

In the Western World, the major suppliers of gallium are Alcoa, Alusuisse and VAW, all of whom have accumulated many years of experience in the technology of extracting gallium from bauxitic ores as a by-product of their alumina production. Alcoa has produced gallium for many years using proprietary technology, and is believed to supply about 5-6 metric tons per year. In 1974, Alcoa reported a technological breakthrough¹³ enabling them to increase significantly their production capacity of high-purity gallium; and in 1975 they announced the start-up of a new gallium extraction facility at its Mobile, Alabama alumina plant as well as at its Bauxite, Arkansas plant capable of producing 50 to 1,000 grams ingots.

Alusuisse and VAW are the key Western European suppliers of gallium with purities ranging up to 99.9999%. They have published extensive sales literature; and in

cooperation with Pechiney in France and Sumitomo in Japan, it is believed they sell worldwide 8-9 metric tons of gallium per year to end users.

In the United States, Eagle-Picher Industries produce gallium metal as well as gallium oxide and trichloride from its zinc production at its Quapaw, Oklahoma facility. Canyonlands 21st Century Corporation reprocesses gallium from gallium arsenide at its plant in Blanding, Utah. Kawecki-Beryllco also supplies gallium, but they are not primary producers. However, they have recently formed a company, Ingal International Gallium GmbH., with VAW in Germany to produce gallium with VAW technology and with a plant capacity estimated at 2-3 tons per year. The other major aluminum companies in North America, Reynolds Metals, Kaiser Aluminum and Alcan, do not recover gallium.

Gallium supply and production capacity from the Eastern bloc countries are not known. On the basis of patent literature, plants for extracting gallium from bauxite exist in Russia, Czechoslovakia, and Hungary; and it has been reported that the annual Hungarian production is 100-200 kilograms per year¹⁴.

3.3.3 Availability from Bauxite

a. Primary Aluminum Production

A realistic estimate* of the present potential availability of gallium by extraction from the sodium aluminate liquor in aluminum ore processing can be obtained from the recent history of primary aluminum production from bauxite throughout the free-enterprise world (excluding the Soviet Union and Sino-Soviet bloc countries). These data are given in Table IV in thousands of metric tons (2,205 lbs.) for the five year period, 1974-1978, which includes an economic recession (1974-1975). It may be seen that the primary aluminum production has increased only 4.5%, from 10,931,000 to 11,427,000 metric tons; and the United States, Canada, and the Western European and East Asian blocs of countries accounted for approximately 87% of the total production. The bauxite requirements to produce the primary aluminum in 1978 would be about 46,000,000 metric tons, since production of a ton of aluminum generally requires at least four tons of bauxite. Commercial grade bauxite ores contain at least 45-50% alumina (Al_2O_3) which, in turn, has 52.9% aluminum.

On the reasonable assumptions that the weight ratio of gallium to aluminum in bauxite is 2.4×10^{-4} (average gallium content of 0.006%) and that 50% of the gallium on the average is lost in the red mud residue during ore processing, then approximately 1,370 metric tons of gallium were potentially available in 1978 by present extraction technologies. Since the free-enterprise world production capacity of gallium is estimated to be 25 metric tons, less than 2% of the bauxite used in 1978 for producing primary aluminum would have been processed for gallium extraction.

Recent projections place the free-enterprise world primary aluminum production in 1985 at 17.4 million metric tons. This could provide a potential gallium source of approximately 2,100 metric tons, if all the bauxite used to produce primary aluminum were processed for gallium extraction using the above assumptions.

It is apparent from the foregoing that gallium availability from bauxite in 1978, as a by-product of primary aluminum production, is more than enough to meet present as well as immediately foreseeable demands. However, the widespread use of gallium arsenide in photovoltaic cells could change the demand situation dramatically; and in particular, if these semiconductor devices were used in satellite power systems now under study by NASA. In the most recent conceptualized design for one 5 GW satellite power system, it is estimated that 390 metric tons of gallium would be required. This represents about a 1,600% increase over present free-enterprise world production capacity, and 28% of the potentially available gallium (1,370 metric tons) from the

*This represents a conservative estimate, since it is recognized that gallium can also be recovered from bauxite, which is processed solely for non-metal used of alumina.

bauxitic ores currently processed to produce primary aluminum. The development of a network of such satellite power systems would necessitate an essentially new gallium recovery industry. For economic reasons, it would have to be closely coupled with alumina and primary aluminum producers, and would necessitate accelerated efforts in recycling of gallium. The potential gallium recovery from zinc, lead and copper ores would be considerably less because of the much smaller tonnages involved. The recovery of gallium from selected coals would require a new technology to be cost competitive, and this is not realizable in the foreseeable future.

TABLE IV. PRIMARY ALUMINUM PRODUCTION IN THE WORLD*
(Thousands of Metric Tons**)

	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>
United States	4,448	3,519	3,857	4,117	4,358
Canada	1,006	883	628	976	1,051
Europe	3,150	3,064	3,150	3,292	3,345
East Asia	1,167	1,060	963	1,235	1,126
South Asia	296	329	402	379	385
Oceania	330	323	372	393	414
Africa	278	271	337	367	336
Latin America	<u>256</u>	<u>273</u>	<u>316</u>	<u>358</u>	<u>412</u>
Total	10,931	9,722	10,025	11,117	11,427

Area Definitions:

Europe (Austria, France, Germany, Greece, Iceland, Italy, Netherlands, Norway, Spain, Switzerland, Sweden, United Kingdom)

East Asia (Japan, South Korea, Taiwan)

South Asia (Bahrain, Turkey, India, Iran)

Oceania (Australia, New Zealand)

Africa (South Africa, Cameroon, Egypt, Ghana)

Latin America (Argentina, Brazil, Mexico, Surinam, Venezuela)

* Free Enterprise Countries

** Metric Ton equals 2205 lbs.

Source: International Primary Institute

b. Bauxite Production, Reserves, and Resources

Data on commercial bauxite production and reserves in 1978 throughout the world are given in Table V in millions of long tons (2,240 lbs.). Approximately 65% of the world bauxite comes from four countries: Australia, Guinea, Jamaica and Surinam. Three of these also have large commercially-proven reserves. The United States, which is the major producer of primary aluminum (see Table IV) has a domestic production of 1.7 million tons only. Consequently, it depends heavily on foreign sources of bauxite largely from Jamaica, Surinam, Guyana, the Dominican Republic, Haiti, and Guinea. Imports from Australia and Brazil are expected to increase significantly over the next decade.

Australia has replaced Jamaica as the major producer of bauxite with 26.5 million long tons in 1978. This is a major development since in 1960 it had produced only 0.97 million tons. Its production rate has been increasing rapidly reaching about 1 million tons in 1965 and 9 million tons in 1970. With this type of commitment, in addition to its dominant position in bauxite production for years to come, thereby insuring a politically reliable supply of bauxite. Australia is also fast becoming one of the leading aluminum smelting centers and, hence, could become a major gallium producing center.

Guinea has also passed Jamaica, and is now the second major bauxite producer with 17 million long tons, which is double the production in 1974. This rapid expansion, which reflects its enormous commercial reserves of 8,200 million long tons, is expected to continue.

Jamaica, which was the major bauxite producer for many years up until 1972, is now the third leading supplier. Many of its principal mines have been wholly or jointly owned by the major North American aluminum companies (Alcoa, Reynolds and Kaiser). As a result, Jamaica has been and continues to be the chief source of bauxite imports to the United States, accounting for over 55% of the total imports in 1974 according to the Bureau of Mines¹⁵. This represents 50% of the total bauxite consumed in the United States. This level of imports will probably decline due to the political upheavals in Jamaica over the past decade, and the increased attractiveness and availability of bauxite from Australia, Guinea and Brazil.

Significant deposits of bauxite have been found in the northern regions of Brazil, which now has commercial reserves greater than Jamaica. Although its bauxite production was only 1 million long tons in 1978, development of these relatively new deposits should make Brazil one of the five major suppliers within the next five years. Increased production from India, with reserves of 1,600 million tons, can also be expected between 1980-1990. Significantly, a strong enrichment of gallium with aluminum in Indian Bauxite on basalts has been reported¹⁶.

Surinam, Greece and Guyana are also significant suppliers of bauxite. However, their production has been relatively constant over the past decade, presumably reflecting a strategy to avoid rapid depletion of their moderate reserves. This would be particularly true in the case of Greece and Surinam. The United States imported 2.8 million long tons of bauxite from Guyana and Surinam in 1974. This represented 20% of its total imports, and a level second only to Jamaica¹⁷.

Table V shows that the total of known commercial reserves of bauxite are 26,880 million long tons, which represent a four-fold increase over the past 15 years and a 320 year supply at the 1978 production level of 84 million tons. Cumulative demand for bauxite is expected to be 3,000-4,000 million tons by the year 2000, which is still only 13% of current commercial reserves. Hence, no future bauxite shortage can be expected over known reserves even at an unanticipated acceleration in future bauxite consumption.

TABLE V. COMMERCIAL BAUXITE PRODUCTION AND RESERVES IN 1978.
(MILLIONS OF LONG TONS¹)

	<u>1978 Production</u>	<u>% of Total</u>	<u>1978 Reserves</u>	<u>% of Total</u>
United States	1.7	2.0	40	0.2
Australia	26.5	31.5	6,400	23.8
Brazil	1.0	1.2	2,500	9.3
Greece	3.0	3.6	750	2.8
Guinea	12.0	14.3	8,200	30.5
Guyana	3.0	3.6	1,000	3.7
India	1.5	1.8	1,600	6.0
Jamaica	11.4	13.6	2,000	7.4
Surinam	5.0	6.0	490	1.8
Other Market Economies ²	6.7	7.9	2,800	10.4
Hungary	3.0	3.6	300	1.1
Soviet Union	4.7	5.6	200	0.8
Other Central Economies ³	<u>4.5</u>	<u>5.3</u>	<u>600</u>	<u>2.2</u>
Total	84.0	100.0	26,880	100.0

1. Long Ton equals 2,240 lbs.

2. (France, Italy, Yugoslavia, Dominican Republic, Haiti and others)

3. Sino-Soviet Bloc Countries, Mostly China

Source: U. S. Department of Interior
Bureau of Mines
Commodity Data Summaries, 1978

Table VI shows data on the most recent estimates of bauxite resources in the major regions of the world and the United State. These resources include the commercial reserves listed in Table V in addition to sub-economic and expected, though as yet undiscovered, reserves.

TABLE VI. ESTIMATED WORLD BAUXITE RESOURCES
(MILLIONS OF LONG TONS*)

United States	300 - 325
Caribbean & Central America	3,000 - 4,000
South America	8,000 - 10,000
Europe	2,000 - 3,000
Africa	12,000 - 15,000
Asia	7,000 - 9,000
Oceania (Australia and New Zealand)	<u>8,000 - 9,000</u>
Total	40,000 - 50,000

* Long Ton equals 2,240 lbs.

Source: U. S. Department of Interior
Bureau of Mines
Commodity Data Summaries, 1978

The large contribution from Africa will come mainly from Guinea, Oceania, from Australia; Asia, from India; and South America, from Brazil and Guyana.

Fig. 3 shows the distribution of bauxite deposits around the world in accordance with accepted classifications¹⁷: (1) on igneous and metamorphic rocks, (2) on sediments (carbonate rocks and clastic strata and (3) on clastic bedrock. These deposits include commercial ores and reserves.

Fig. 3 Distribution of bauxite deposits of the world (after Patterson, 1967), reference no. 17.

4 CONCLUSIONS

1. The 5 GW satellite power system using gallium arsenide solar cells, now under study by NASA, would require 390 metric tons of gallium. This represents a 1,600% increase over present free-enterprise world production capacity (25 metric tons), and 28% of the potentially available gallium (1,370 metric tons) from bauxitic ores currently processed to produce primary aluminum. A network of such satellites would necessitate an essentially new gallium recovery industry, which would have to be coupled closely with the aluminum industry for economic reasons.
2. The major market for gallium is the electronics industry, which requires the metal in its highest form of purity (99.9999%). The price for this grade of gallium is now \$525/kg.
3. In the free-enterprise world, the major suppliers of primary gallium are Alcoa in the United States and Alusuisse and VAW in Western Europe. These companies account for over 90% of the free world supply of gallium to meet current market needs.
4. The free-enterprise world consumption of gallium is estimated to be 14,000 kg., and is not expected to increase significantly over the next few years despite the emergence of new electronic applications requiring gallium compounds. Since the free world production capacity of gallium is about 25,000 kg., then an over-supply situation now exists. This could be dramatically reversed with the widespread use of gallium arsenide photovoltaic cells in future terrestrial and space power systems.
5. The primary source of gallium is bauxite ores containing 0.003-0.009% gallium and these ores account for over 90% of the world supply of gallium. Commercial processes for extracting the gallium from bauxite involve both direct electrolytic and wet chemical methods, which provide extraction efficiencies of 30-50% and the potential for efficiencies as high as 80%. Definitive data on the cost comparison of these processes are not available.
6. The world-wide commercial reserves of bauxite total 26,880 million long tons, which represent a 320 year supply at the 1978 production level of 84 million tons. Estimated cumulative demand for bauxite by the year 2000 is still only 13% of current commercial reserves.
7. Data on the primary aluminum production from bauxite throughout the free-enterprise world suggest that approximately 1,370 metric tons of gallium were potentially available in 1978 by present extraction technologies and assuming an average content of 0.006% Ga in bauxite. Since the world production capacity of gallium is estimated to be 25 metric tons, less than 2% of the bauxite used in obtaining alumina for primary aluminum production was processed for gallium extraction.
8. Australia is now the major producer of bauxite with 26.5 million long tons in 1978. Its abundant commercial reserves serve to insure the free-enterprise world supply of bauxite for years to come. Guinea is the second major producer with 17 million long tons followed by Jamaica, which was the major bauxite producer until 1972. With its new discoveries of bauxite ores, Brazil may become a major producer within the next five years.
9. The United States, which is the major producer of primary aluminum, depends heavily on foreign sources of bauxite principally from Jamaica (55% of imports), Surinam, Guyana, the Dominican Republic, Haiti and Guinea.
10. Commercial extraction methods can provide gallium with a purity of 99.9%. Conversion of this grade gallium to the high purity (6 nines) form requires additional processing, which raises the gallium price by at least \$100/kg.

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