New demand puts tension into gallium/indium supply chain

As orders have picked up from the 2008-2009 financial crisis, strain has been put on compound semiconductor raw material supplies. Now, China may be planning stockpiles that could further restrict access to indium and gallium. Mike Cooke reports.

The materials indium and gallium have a growing range of applications. Although both are widely used in compound semiconductor devices, the use of indium extends greatly beyond this sphere. In fact, the most widespread use of indium is in ITO (indium tin oxide) transparent conducting layers, as applied in flat-panel displays, touch screens, smart-phones, high-efficiency solar panels and high-efficiency, long-life LED lighting (both for LCD back-lights and, in the future, more general applications).

Also some of these applications are dependent on indium and gallium semiconductor technology to work at all. For the emission of long-wavelength light, i.e. red-orange-yellow (ROY), various combinations of indium gallium arsenic and phosphorous (InGaAsP) are used. The shorter wavelengths — green, blue, violet and beyond — are covered by indium gallium nitride (InGaN) compound semiconductors.

Aluminum (Al) (another group III metal) also has uses in both regimes (particularly for high-brightness ROY light emission in the forms AlGaAs and AlInGaP), but is not a concern in supply terms, being relatively easy to extract in large quantities from bauxite. The purpose of aluminum is generally to shorten the wavelength through widening the bandgap of semiconductor layers, and also for barriers in quantum well structures.

Indium and gallium also find use in light absorption/solar cell active layers, both in the combinations already mentioned (high efficiency, but high cost) and in the lower-cost copper indium gallium diselenide (CIGS) form [Mike Cooke, Semiconductor Today, vol4, issue 3, p88, April/May 2009].

At present, the greatest demand for high-brightness LEDs (HB-LEDs) is for those used as backlights in LCD TVs/displays (marketed as 'LED TV' by manufacturers), replacing more traditional technologies such as cold-cathode fluorescent lamps (CCFLs). The switchover is allowing LCD manufacturers to produce thinner panels that operate on a lower energy budget. Other advantages include a brighter display, better contrast and cooler running.

The LEDs used in such units can be 'white' or 'RGB'. The 'white' flavor refers to a blue InGaN LED with a yellow phosphor material such as cerium-doped yttrium aluminum garnet (Ce:YAG) that produces an approximation to white. The 'RGB' option is more expensive, but gives a better-quality result. RGB LED systems use combinations of separate red, green and blue LEDs to achieve a full-color result with truer blacks, whites and color rendering performance (color gamut).

Market research firm Display Search believes that more than 50% of LCD TVs will be LED-backlit next year. In 2014, they will account for more than 80% of shipments on the market researcher's most recent assessment (Figure 1).

By 2014, another researcher, Strategies Unlimited, puts the HB-LED market at $19bn, representing a 30% compound annual growth rate (CAGR) over 2009 [High-Brightness LED: Market Review and Forecast 2010]. For particular applications, such as signs/displays and illumination, the expected CAGRs are even higher (61% and 45%, respectively). For more general illumination and signage, further attractions of HB-LEDs include lower power consumption and longer operating lifetimes (up to 50,000 hours, versus 10,000 hours for compact fluorescent or 2000 hours for incandescent).

Raw material pricing

However, such new LED production activity feeds demand back down the supply chain and puts pressure on raw material prices. Many semiconductor producers are used to being able to beat down materials prices because substances such as silicon are as common as muck (or at least rock and sand). With HB-LEDs the situation is different — practically all devices use the very rare metals indium and gallium. However, even here Taiwanese manufacturers have been able to bargain until recently.

A big change in the balance of power has come from "competitors backed by huge corporations, such as Samsung and LG, much better positioned to absorb higher material costs and to guarantee their supply in a constrained market", says the market research firm Strategy Analytics. In May, Strategy Analytics was warning of a shortage of key semiconductor materials in second-half 2010 ['Materials Shortage to Restrict Rampant LED Market', Strategy Analytics, 2010].

In the near-term, the firm was predicting a 20% rise in trimethyl-gallium (TMG) prices. This material is the precursor source for Ga used most commonly in the metal-organic chemical vapor deposition (MOCVD) process generally employed for nitride semiconductor hetero-structuring.

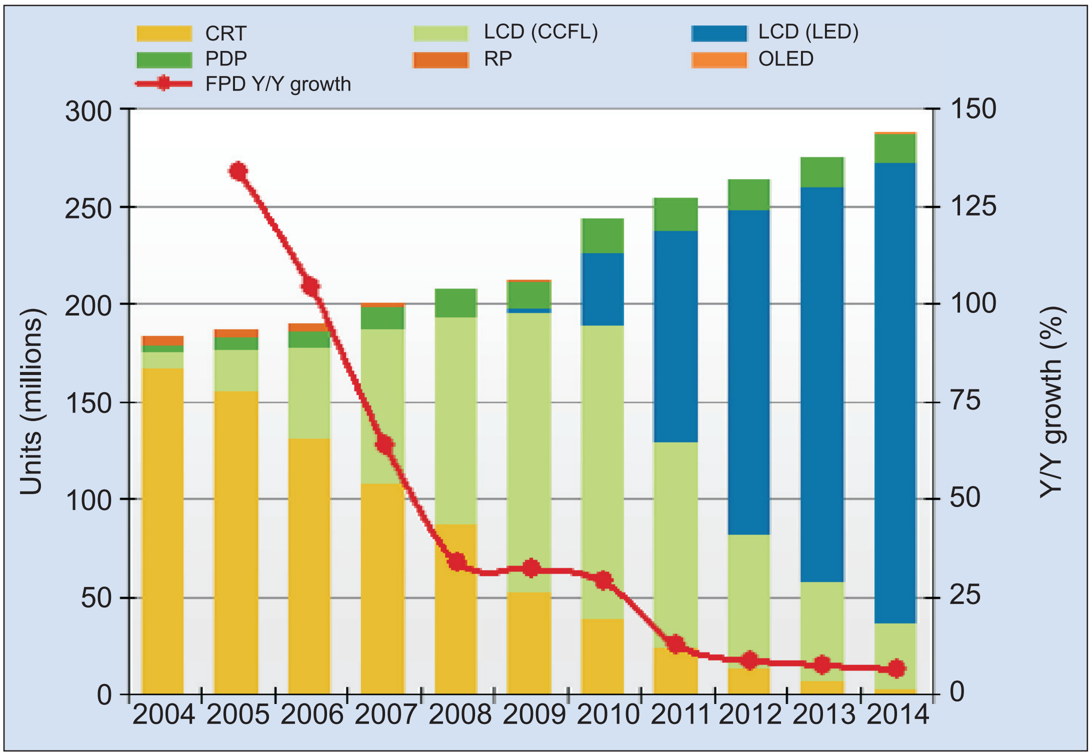

Figure 1. Worldwide TV market by technology. Source: DisplaySearch Quarterly Advanced Global TV Shipment and Forecast Report, Q3, 2010.

TMG prices have gone from a couple of dollars per gram to $10/g earlier this year, before settling to a more comfortable $3–4/g. The supply of the sapphire base wafer was also cited as being in short supply.

These concerns come on top of those connected with sharply increased demand coming recently from China for MOCVD growth reactors [Mike Cooke, Semiconductor Today, vol5, issue 7, p90, September 2010].

Other epitaxial techniques use liquid- or vapor-phase, or even molecular beams, to produce semiconductor layers. The source materials in these cases are much simpler, or even elemental species.

Metal-organic precursor suppliers expand

A number of companies are currently rushing to meet the TMG shortfall: AkzoNobel, Albemarle, Chemtura, Dow Electronic Materials and SAFC Hitech have all this year announced planned expansions of metal-organic (MO) capacity for group III metals (see news pages 32–33 of this issue).

Steven Entwistle, VP of the Strategy Analytics Strategic Technologies Practice, commented in May: "Capacity expansions already in progress should relieve these constraints by mid-2011. Until then, the average selling price (ASP) of high-brightness LEDs based on gallium nitride should hold up well."

Dow in fact made two announcements, one this November concerning breaking ground for a new facility in Korea, and another in June covering more general plans for expanded production of TMG. The company has been adding 'significant TMG capacity' to its facilities in the USA to meet short-term demand. The Korean facility is expected to come online in early 2011 (probably Q2), aimed at meeting longer-term demand. At the end of the multi-phase plan, Dow says that it will have a total TMG capacity of 60 (metric) tons/year. In future, the firm also expects that other metal-organic chemicals will be available from Korea.

A Korea production site is convenient both for customers in that country and also for other nations of the Asia-Pacific region such as Taiwan where much LCD and semiconductor production is carried out. Dow Electronic Materials is the biggest supplier of TMG to Korea and sees itself as the leading supplier of precursors to the LED market as a whole and has patented precursor manufacturing processes and delivery technology.

Expanded high-purity metal-organic capabilities are also among the aims of a Korean investment by US company Albemarle, announced in September. The company presently produces TMG in the USA, and the new Korea facility is expected to 'mirror' this capability. The facility will begin with TMG purification in early 2011, adding in other capabilities through next year.

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In August, the US company Chemtura signed a memorandum of understanding for a metal-organic

Table 1. Average year-end prices for In and Ga. Source: US Geological Survey, Mineral Commodity Summaries, January 2010.

$/kg	2005	2006	2007	2008	2009
Indium					
Indium Corp 99.97%	946	918	795	685	500
New York dealer 99.99%	961	815	637	519	390
Gallium					
Average for 99.9999% & 99.99999% US import	538	443	530	579	480

Table 2. World indium refinery production in metric tons. Source: US Geological Survey, Mineral Commodity Summaries, January 2010.

	2008	2009e
Belgium	30	30
Brazil	5	10
Canada	45	50
China	310	300
Japan	65	60
Korea, Republic of	75	85
Peru	6	20
Russia	12	12
Other countries	25	30
World total (rounded)	**570**	**600**

joint venture with Korean company UP Chemical. The Korea-based JV would manufacture and sell high-purity metal-organics such as trimethyl-aluminum (TMA), along with TMG (up to 30 ton/year TMG capacity is expected). Supply is due to begin in December 2010, with a fully integrated manufacturing capability being established at the Korean site for TMG and TMA in late 2011. Again, the focus will be on supplying South Korea and Asia-Pacific more generally, hoping to pick up on the expected HB-LED bonanza.

Chemtura also has a subsidiary based in Germany — Chemtura Organometallics GmbH — where TMA production is to be added to an existing facility for producing diethyl-zinc (DEZ), which is a substance used as a polymerization catalyst. The TMA product line will become operational in 2012, the company says.

Netherlands-based AkzoNobel plans to double TMG capacity at its Texas-based facility, with the new production volume becoming available in February 2011. "The capacity addition will further enhance AkzoNobel's position as the leading global producer of this material," the firm says. This comes on top of the firm previously announcing a doubling of its TMG production in May 2010. AkzoNobel also produces indium-, aluminum-, zinc- and magnesium-based metal-organics.

The firm's US operation had been under Chapter 11 bankruptcy protection since March 2009 due to the global recession. Plans for reorganization have been accepted by the relevant court and the firm emerged from Chapter 11 protection in November 2010.

SAFC Hitech was another company investing in increased TMG production with $2m funding at its UK manufacturing facility in Bromborough. Some money for the project came from local government and development agencies. Again the immediate focus is support of HB-LED production.

Now, at the beginning of December, SAFC Hitech too has also announced a further expansion for the Asian market, this time at its plant in Kaohsiung, Taiwan (see news pages). The firm plans to build a dedicated facility for transfilling, technical service and production of LED and silicon semiconductor precursors (to be operational by late 2011).

Another way to expand production has been followed by Korea's Lake LED Materials gaining investment from process materials supplier ATMI, giving the US firm a minority interest. Lake LED Materials is a start-up with capabilities for producing TMG (24 ton/year, according to http://english.etnews.co.kr/news/detail.html?id=201011040009), trimethyl-indium (TMI), TMA, triethyl-gallium (TEG), bis-cyclopentadienyl-magnesium (Cp_2Mg), and other metal organics. ATMI says that it will "help accelerate commercial LED materials introductions, with select marketing and technology rights".

Sources and costs of raw materials

A large part of the high cost of these materials is down to the rarity of the source metals. In the past five years (Table 1), indium prices have ranged from almost $1000/kg down to less than $400/kg. Gallium has been somewhat more stable, at around $500/kg. These are year-end figures and prices for indium have in some periods exceeded $1000/kg. The price fell dramatically following the 2008 economic crash, but improving economic conditions subsequently pushed indium prices to about $600/kg in November 2010.

In 2009, world primary production of gallium was estimated to be 78 tons, down from the previous year's 111 tons [US Geological Survey, Mineral Commodity Summaries, January 2010]. The refined gallium estimate was 118 tons. This latter figure includes scrap recycling. Capacity figures are 184 tons for primary production, 167 tons for refining, and 78 tons recycling. The USGS also gives refinery production figures for indium of 600 tons in 2009 (Table 2).

The main source for gallium is from the aluminum ore bauxite, where the USGS estimates the gallium content of world deposits to be more than a billion kilograms. However, further deposits of gallium could be associated with zinc ores. These estimates assume a gallium concentration in bauxite of 50 parts per million. The concentration in zinc ore is the same. However, this material can only be accessed if the deposit is economic. This would depend both on the viability of the respective ores for their primary product (aluminum or zinc) and on trace metal extraction capability. The USGS comments that only a small percentage of gallium in these ores is ‘economically recoverable’.

The main indium source is sphalerite, a zinc sulfide ore. The indium concentration in these deposits ranges from 1ppm to 100ppm. Although indium occurs in higher concentrations in some tin and tungsten vein stockwork deposits, these sources are difficult to process for indium extraction in an economic fashion.

Another possibility has been raised recently by South American Silver Corp. The firm has been performing exploratory drilling at Malku Khota, Bolivia. The site has been qualified under the Canadian National Instrument 43-101 mineral resource classification as having an indicated resource of 144.6 million ounces of silver and 845 ton of indium plus an inferred resource of 177.8 million ounces of silver and 968 ton of indium.

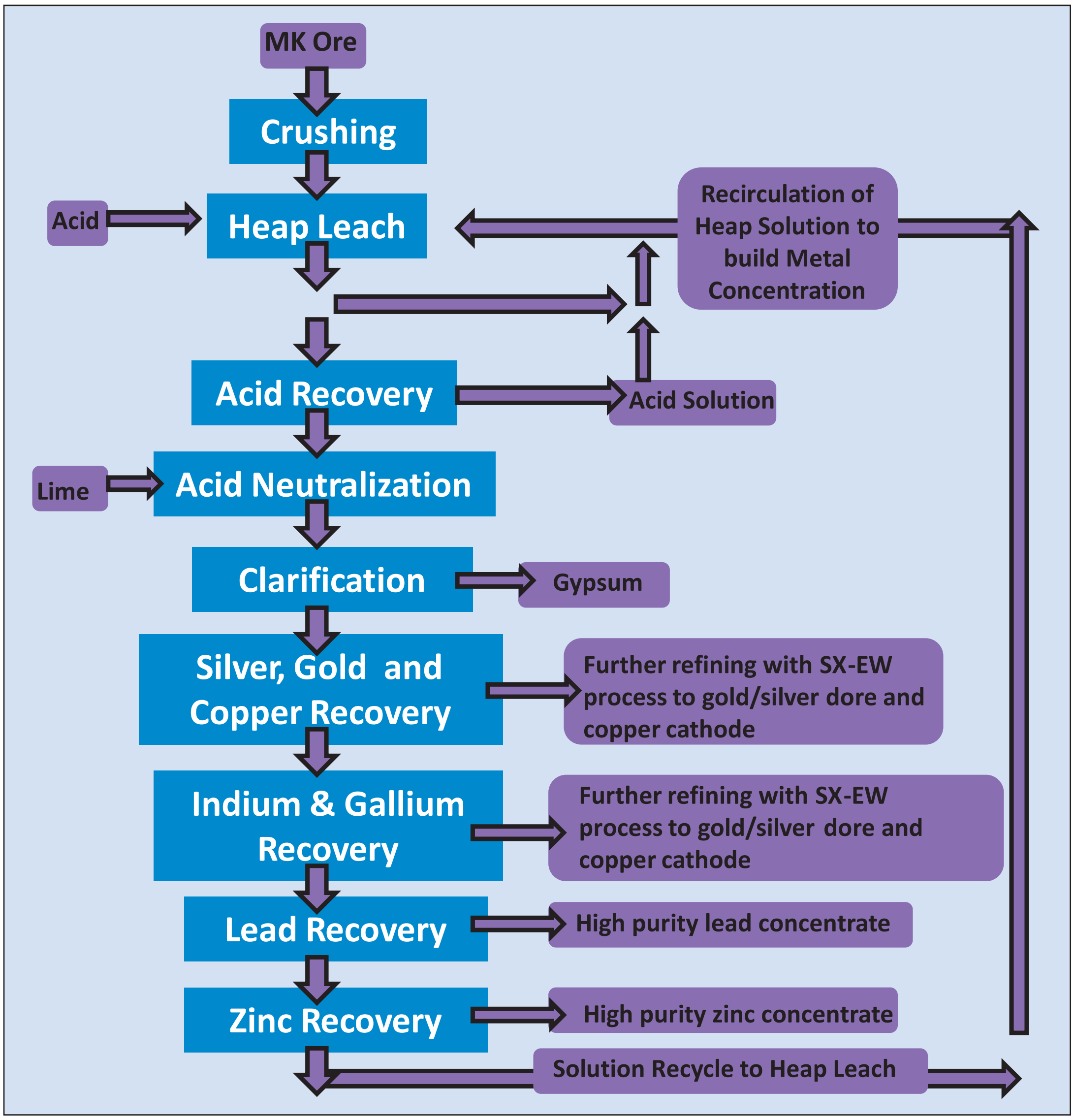


Figure 2. Metallurgy flow sheet for proposed acid-chloride leach process.

The two best intercepts of this drilling with the minerals at the site give indium contents of 2.7ppm (=grams/ton) and 1.4ppm. The figures for gallium are in fact higher, at 3.6ppm and 3.2ppm.

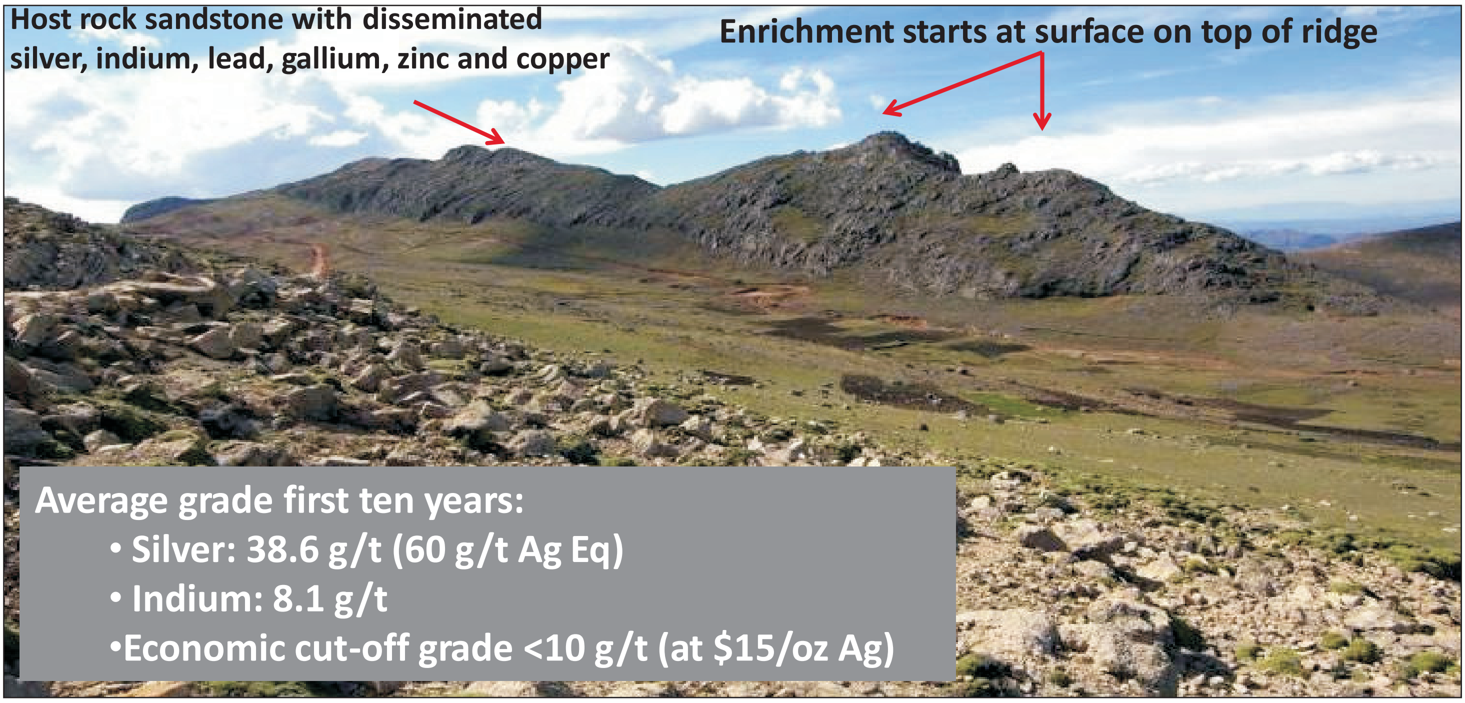
The firm reports that it has carried out metallurgical and process-related test work to refine leach recovery characteristics for silver and indium and associated gold, copper, lead, zinc and gallium mineralization (see Figure 2). The Third Quarter President’s Message and Project Update comments: “The test work to date indicates the amenability of heap leaching and/or milling of the mineralized material at Malku Khota.”

In copper mining, leaching is used to dissolve the desired material in a solvent, which is then subjected to ‘electro-winning’ (i.e. electrolysis). South American Silver sees this as a possibility for recovering indium from its silver ore. Another possibility is to gather the indium as part of the silver refining process, similarly to the techniques used in zinc smelting.

The firm says that it is “committed to upholding high environmental and social standards while focusing on delivering the financial growth its shareholders expect”. The Altiplano region of Bolivia (where Malku Khota is situated) has been involved in large-scale mining since the Spanish conquest of the Incas (who knew of the silver deposits).

The traditionally highly exploited local population has been exposed to the heavy-metal pollution that can arise from such operations. Some effort is presently being made (not directly connected with South American Silver’s explorations) by the French Institut de Recherche pour le Développement (IRD) public research institute to assess the level and effect of pollution in the area [http://en.ird.fr/the-media-library/scientific-news-sheets/357-the-impact-of-mining-in-bolivia].

In terms of present sources for gallium and indium, China figures prominently. For gallium the main producers are China, Germany, Kazakhstan, and Ukraine. China is also responsible for about half of the world’s production of indium (Table 2). Of US gallium imports



Mineralization at Malku Khota, Bolivia, showing sandstone rocks bearing indium and gallium deposits.

(29 tons in 2009), the USGS reports that 24% comes from Germany, 20% from Canada, 16% from China, and 12% from Ukraine, with 28% emanating from 'other' sources. For indium (95 tons), the US is more reliant on China (40%), with the remainder from Japan (19%), Canada (18%), Belgium (7%) and 'other' (16%).

While the US government does not maintain stockpiles of either indium or gallium, other nations do. In particular, Japan Oil, Gas and Metals National Corporation (JOGMEC) announced plans to set up stockpiles of 42 days worth of standard national consumption of these metals in 2009. Korea set up rare-metal stockpiles in 2006, and announced plans to increase this activity in the period up to 2016.

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The US edition of China Daily reported in November 2010 (based in turn on Shanghai Securities News report involving 'unnamed sources') that indium and gallium were among ten rare metals that the State Bureau of Material Reserve was considering for stockpiling to stabilize supply and prices. At about the same time, the China Securities Journal reported moves by China's Commerce Ministry to place stricter controls on rare-metal exports — a 2–3% cut in quotas per year, according to more 'unnamed sources'.

Such developments have raised concerns that China is moving to withhold shipments of materials for political reasons. The 31 Japanese importers of rare-earth materials reported disruptions in shipments recently in a Japanese finance ministry survey. In the recent case of rare-earth shipment disruptions in Japan and the USA, some suspect the shortages are due to a territorial dispute (Japan) and a trade disagreement (USA) with China. The October shipments from China fell by 77% from the previous month's volume.

The Chinese government has denied such charges and says that it would not use its near-monopoly in rare earths as a bargaining tool. China also points out that it introduced the rare-earth restrictions in 2006 to minimize the harmful effects on the environment of mining such materials. Indeed, pollution concerns have restricted the amount of rare-earth extraction elsewhere in the world. In China, long-term unlicensed, indiscriminate extraction practices — in addition to wasting national resources — have seriously damaged ecosystems near mining operations.

One alternative to aggressive increases in mining is the recycling of waste that contains these materials. In May, the United Nations Environment Programme (UNEP) called for "rapid improvements in the recycling rates of so-called 'high-tech' specialty metals like lithium, neodymium and gallium" [http://hqweb.unep.org/Documents.Multilingual/Default.asp?DocumentID=624&ArticleID=6564&l=en&t=long].