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## The scarcity of materials.

Over the last few years there have been some concerns about the availability of certain materials (1). The ones hitting the news include indium and the rare earth as a whole group of materials. Indium is of interest because of the need for transparent conducting coatings for the display industry as well as more recently in copper indium gallium diselenide (CIGS) photovoltaics as well as for the transparent electrodes of the devices. The rare earth group includes neodymium as used in strong magnets, erbium for doping optical fibres, tellurium for CdTe solar cells, hafnium oxide that can be used as an insulator or can be used in semiconductors and can outperform silica, tantalum that is used in high density storage capacitors, dysprosium that can change shape in magnetic fields as in magnetostriction, technetium as used in medical imaging, lanthanum & cerium that can be alloyed to make mischmetal to make one of the electrodes in batteries, europium & terbium that have phosphorescent properties and are used in displays as well as to modify the colour in the low energy light bulbs, rhenium that can be alloyed for use in superalloys in jet engines.

A list ranking the 52 materials at most risk has been developed (1) where it shows that China is the global leading supplier of 27 of the 52 elements listed. The risk is evaluated using four factors; scarcity, production concentration, reserve base distribution and political stability. The political stability can vary widely depending on the country and what news stories are around at the time. When China stopped all exports of rare earths to Japan because of the arrest of a Chinese boat Captain the risk level increased. If China could do that to Japan it could do the same to anyone else for anything else that did not meet with their approval. This type of blackmail is also observed by many other governments, some of which are not as stable and may seek to increase their political standing or negotiating leverage by using mineral starvation as a political tool. The rest of the risk calculations are subject to the usual calculation errors. One can only estimate the reserves for known mines and declared ore strikes. This can change as the incentives to go exploring increase with price increases.

Users of some scarce materials are working to optimising their alloy compositions as well as developing the manufacturing process to minimise the quantities required. As a result of the supply limitations and price rises a number of mines are being reactivated and new mines are being sought in alternative world locations. The University of Tokyo has found mineral concentrations in 78 locations in seabed mud at depths between 3,500 - 6,000m (2). At least a third of these sites had high proportions of rare earths present. There are sites both east and west of Hawaii and east of Tahiti. The Pacific Ocean floor is proving to be of great interest and many mining companies are exploring opportunities. Much of the work is funded by countries concerned about restrictions and an over reliance on China as the current dominant supplier. This ocean floor activity is already raising concerns about the massive ecological damage that could be caused particularly if the mining is unregulated. Simplistically if one looks at the Earth the crust is less than 1% of the total volume of the Earth but this volume is huge at around 1 x 10<sup>10</sup> cu km. The scarce materials make up a small proportion of the crust volume it still gives a huge potential volume of the order 10 x 10<sup>6</sup> cu

km available. Of course much of this will be in inaccessible places and in such small concentrations that it is too expensive to extract. However, the volume does suggest that the materials have not really been exhausted but simply the locations have not yet been found. The other encouraging fact is that for many of these materials that we are regarding as scarce the amount recycled is minimal. Other materials such as aluminium, copper, lead, tin and iron recycling is commonplace. After the massive price rise for Indium a few years ago this too is now recycled in significant quantities. However for the rare earths it is believed the recycling rate is less than 1%.

There have been some studies on the disposal of mobile phones, portable computers (PCs) and other commonplace circuit boards and it has been calculated that 1 tonne of electronic scrap from PC's contains more gold than from 17 tonnes of gold ore. If you then add in the other materials that typically appear on PC circuit boards such as Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Ga, Fe, Pb, Mn, Hg, Pd, Pt, Se, Ag, Zn & it becomes a rich source of materials (if a little hazardous). I am not sure that anyone has done such a detailed study of the lifetime, disposal routes and potential recycling costs and analyzed the size of the benefits available for recycling rare earths. I would expect that compared to trying to mine the deep sea bed there has to be economic advantages to recycling.

One aspect that seems to be ignored is the energy cost of extraction and refining. As various materials become scarce the difficulty and energy required to extract and refine from lower concentration ores is likely to increase. This coincides with the decline in availability and increasing cost of fossil fuels. Coupled to this is a reluctance to invest in nuclear energy power stations because of various well publicised accidents. Although there have been many predictions on how alternative energy sources can supply our needs I am not sure this includes the large increases in energy that may well be required to keep the supply of materials flowing easily.

## Indium

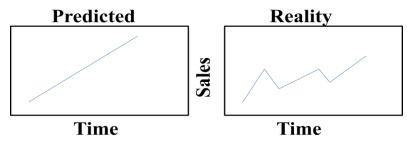
Indium is one of the major stories of interest regarding scarcity of materials. Indium tin oxide (ITO) has been the dominant transparent conducting coating used in the display industry for many years. The growth of the display industry has been predicted to be large enough that this industry alone could consume all the indium mined each year. Coupled to this there is the photovoltaics industry that is growing even more rapidly than the display industry and is expected to also consume indium at a faster rate than it is being mined. The combination of these two rapidly growing markets has resulted in the indium stockpiles being rapidly reduced over the last few years. This assessment of a future scarcity of indium led to at least one world leading photovoltaic manufacturer opting to stop the development and production of CIGS photovoltaic devices.

Again the fear of industry being limited by the supply of indium has led to alternatives being sought. This has included alternative materials that have been researched such as fluorine doped tin oxide, tin antimony oxide, cadmium tin oxide with aluminium doped zinc oxide (AZO) being the leading contender to be used as a direct replacement. This search for alternative materials has also led to a whole raft of alternatives being developed. Currently none of the solutions are regarded as a universal replacement to ITO but they are regarded as suitable replacements for certain applications. Some of the other alternatives include ITO – wire mesh – ITO where the fine wire mesh is a way of reducing the ITO thickness but maintaining or improving the conductivity. Another group of materials is the conducting polymers of which PEDOT-PSS is one leading the way either as a single coating or as a PEDOT-PSS - wire mesh - PEDOT-PSS sandwich. Again the wire mesh is designed to significantly increase the conductivity without losing too much visible light transmittance. Similar to the woven wire mesh is the inkjet printing of copper in a similar format. The polymer alternatives to ITO have been demonstrated for several years. Somewhat behind in development is the use of nanotubes. These too have been demonstrated both as a single layer coating and using the carbon nanotubes has been shown to be better than for conducting polymers and is expected to be eventually become better than for ITO. The limitation at present is the bulk manufacture, filtering and sizing of the carbon nanotubes. Then following on after the carbon nanotubes is the use of graphene and graphene combined with a metal grid.

This all leads to the conclusion that the future lack of indium is not going to be a problem because there are enough suitable alternatives in the pipeline.

## **Photovoltaics**

Over the last few months there the press have, it seems to me, delighted in announcing the failure of some photovoltaic companies. As with any industry that is growing very rapidly the growth will be erratic with sudden dips and spurts as the market reacts to a variety of announcements both within as well as external to the industry. In the case of photovoltaics this also happens to have coincided with turmoil in world economics. Countries that announced attractive feed in tariffs (FiTs) have had to consider if they can afford the original terms of the FiTs they offered. In some cases they have withdrawn the FiTs, causing large projects to be cancelled. This then had the knock-on effect on PV suppliers which changed their reported financial performance and projected sales. In some cases the governments involved changed their minds and reinstated the FiTs but at a reduced benefit. The aim of this was to encourage suppliers to continue with projects but not to expand the FiT take-up to an unaffordable level. These large solar farm projects being cancelled and reinstated cause suppliers problems. The expectations were based on the supply of PV devices oscillating between over capacity and under capacity very rapidly and the pricing of the PV devices varying accordingly. However when large project were cancelled the supply of devices more typically varied between over capacity and a potentially very large over capacity.



**Figure 1.** The predicted PV growth is always smooth and rapid whereas the reality is anything but smooth. The downturns can be catastrophic for some companies.

The time to purchase and install a PV production line is long and so it is difficult to turn on and off capacity. The result in these short term oscillations can include falls on a growth that remains positive and very rapid as shown schematically in Figure 1. The problem with this unstable market is that in short term downturns companies can make massive losses and even go bankrupt. Some companies fail because their PV manufacturing process is not competitive, either because they have a process that is always going to be more expensive that other competitive processes or because the process has not been developed as far as other suppliers have managed to develop their similar process. Others simply have financial support from backers unwilling to cover the short term losses and wait for the longer term profits.

This problem is becoming larger for any new entry companies into the industry. Now to enter and build a first production line takes a lot on money and this is against a background of competitors already being established in the market place with high yields and plenty of experience. New production lines tend to start with low efficiency and with many inexperienced operators and so it can be a long slow process to achieve high yields. This would suggest that companies who can get past these initial market oscillations will be the ones who will grow larger and will dominate the business in the future. New entries will have an ever higher hurdle to overcome to become established and many will fail or be taken over by the established leaders.

Thus I would suggest the headlines highlighting PV companies going bankrupt are insignificant are misleading and should not merit headlines. They are only part of the noise on a healthy industry that is growing and will continue to do so for many years to come.

- 1. http://www.bgs.ac.uk/mineralsuk/statistics/riskList.html
- 2. http://www.bbc.co.uk/news/world-asia-pacific-14009910