

## Conclusions

Millennial-scale changes are becoming an accepted reality. Initial research concentrated on the massive changes associated with the discharge of sediments and water into the North Atlantic Ocean during the last glacial cycle (marine oxygen isotope stages #2–5) (Figures 1, 2 and 3). However, high-resolution studies of our deglacial world (Figure 4) appear to indicate that similarly spaced but subdued events persist but with very different boundary conditions. A number of publications have also demonstrated that millennial-scale changes in various proxy records are a feature of ocean sediments over at least the last 500 000 years.

The work from tropical and subtropical sites (Figure 2) indicates that Heinrich events have manifestations in ocean reconstructions which belie a simple association with ice sheet instability and collapse. It is far from clear how oceanographic and atmospheric changes are transmitted to the bed of large ice streams, and there is indeed disagreement as to whether the collapse of Northern Hemisphere ice sheets (Figure 2) was regionally coeval or whether the collapses are linked temporally by a mechanism, such as rapid changes in relative sea level. It has, however, been observed that the routing of fresh water (Figure 4) can have dramatic effects, even in the present world, and the key may well lie in a better understanding of the role of the ocean thermohaline circulation system in the global climate system.

## See also

**Cenozoic Climate – Oxygen Isotope Evidence. Thermohaline Circulation.**

## Further Reading

- Andrews JT (1998) Abrupt changes (Heinrich events) in late Quaternary North Atlantic marine environments: a history and review of data and concepts. *Journal of Quaternary Science* 13: 3–16.
- Bond GC and Lotti R (1995) Iceberg discharges into the North Atlantic on millennial time scales during the last glaciation. *Science* 267: 1005–1009.

- Bond G, Showers W, Cheseby M *et al.* (1997) A pervasive millennial-scale cycle in North Atlantic Holocene and Glacial climates. *Science* 278: 1257–1266.
- Broecker WS (1997) Thermohaline circulation, the Achilles heel of our climate system: will man-made CO<sub>2</sub> upset the current balance? *Science* 278: 1582–1588.
- Broecker WS, Bond G, McManus J, Klas M and Clark E (1992) Origin of the Northern Atlantic's Heinrich events. *Climatic Dynamics* 6: 265–273.
- Clarke GKC, Marshall SJ, Hillaire-Marcel C, Bilodaeu G and Veiga-Pires C (1999) A glaciological perspective on Heinrich events. In: Clark PU, Webb RS and Keigwin LD (eds) *Mechanisms of Global Climate Change at Millennial Time Scales*, pp. 243–262. Washington, DC: American Geophysical Union.
- Curry WB, Marchitto TM, McManus JF, Oppo DW and Laarkamp KL (1999) Millennial-scale changes in the ventilation of the thermocline, intermediate, and deep waters of the glacial North Atlantic. In: Clark PU, Webb RS and Keigwin LD (eds) *Mechanisms of Global Climate Change at Millennial Time Scales*, pp. 59–76. Washington, DC: American Geophysical Union.
- Heinrich H (1988) Origin and consequences of cyclic ice rafting in the Northeast Atlantic Ocean during the past 130 000 years. *Quaternary Research* 29: 143–152.
- Hughen KA, Overpeck JT, Lehman SJ *et al.* (1998) Deglacial changes in ocean circulation from an extended radiocarbon calibration. *Nature* 391: 65–68.
- Keigwin LD and Jones GA (1994) Western North Atlantic evidence for millennial-scale changes in ocean circulation and climate. *Journal of Geophysical Research* 99: 12 937–12 410.
- Lowell TV, Heusser CJ, Andersen BG *et al.* (1995) Inter-hemispheric correlation of Late Pleistocene glacial events. *Science* 269: 1541–1549.
- McManus JR, Oppo DW and Cullen JL (1999) A 0.5 million-year record of millennial-scale climate variability in the North Atlantic. *Science* 283: 971–975.
- Sachs JP and Lehman SJ (1999) Subtropical North Atlantic temperatures 60 000 to 30 000 years ago. *Science* 286: 756–759.
- Thomas E, Booth L, Maslin M and Shackleton NJ (1995) Northeastern Atlantic benthic foraminifera during the last 45 000 years: changes in productivity seen from the bottom up. *Paleoceanography* 10: 545–562.

# MINERAL EXTRACTION, AUTHIGENIC MINERALS

**J. C. Wiltshire**, University of Hawaii, Manoa, Honolulu, HA, USA

Copyright © 2001 Academic Press

doi:10.1006/rwos.2001.0036

## Introduction

The extraction of marine mineral resources represents a worldwide industry of just under two billion dollars per year. There are approximately a dozen

general types of marine mineral commodities (depending on how they are classified), about half of which are presently being extracted successfully from the ocean. Those being extracted include sand, coral, gravel and shell for aggregate, cement manufacture and beach replenishment; magnesium for chemicals and metal; salt; sulfur largely for sulfuric acid; placer deposits for diamonds, tin, gold, and heavy minerals. Deposits which have generated continuing interest because of their potential economic interest but which are not presently mined include manganese nodules and crusts, polymetallic sulfides, phosphorites, and methane hydrates.

Authigenic minerals are those formed in place by chemical and biochemical processes. This contrasts with detrital minerals which have been fragmented from an existing rock or geologic formation and accumulated in their present position usually by erosion and sediment transport. The detrital minerals – sand, gravel, clay, shell, diamonds, placer gold, and heavy mineral beach sands – are presently extracted commercially in shallow water. The economically interesting authigenic mineral deposits tend to be found in more than 1000 m of water and have not yet been commercially extracted. Nonetheless, between 1970 and 2000 on the order of one billion US dollars was spent collectively worldwide on studies and tests to recover five authigenic minerals. These minerals are: manganese nodules, manganese crusts, metalliferous sulfide muds, massive consolidated sulfides, and phosphorites. This article will focus on the extraction of these five mineral types.

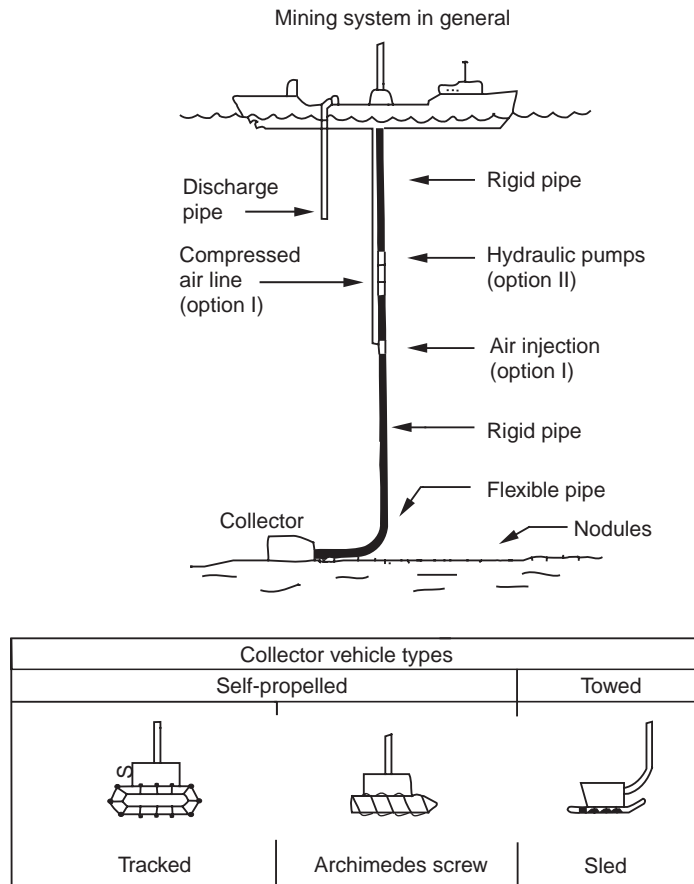
Descriptions of the formation, geology, geochemistry, and associated microbiology of these deposits are presented elsewhere in this work. As a brief generalization, manganese nodules are black, golf ball to potato sized concretions of ferromanganese oxide sitting on the deep seafloor at depths of 4000–6000 m. They contain potentially economic concentrations of copper, nickel, cobalt, and manganese, and lower concentrations of titanium and molybdenum. Manganese crusts are a flat layered version of manganese oxides found on the tops and sides of seamounts with the highest metal concentrations in water depths of 800–2400 m. They are a potential source of cobalt, nickel, manganese, rare earth elements and perhaps platinum and phosphate. Polymetallic sulfides also come in two forms: metalliferous muds and massive consolidated sulfides. The sulfides contain potentially economic concentrations of gold, silver, copper, lead, zinc, and lesser amounts of cobalt and cadmium. The metalliferous muds are unconsolidated sediments (muds) found at seafloor spreading centers and volcanically

active seafloor sites. The metals have been concentrated in the muds by hydrothermal processes operating at and below the seafloor. The best explored site of these metalliferous muds is in the hydrothermally active springs in the central deeps of the Red Sea. By contrast, the massive consolidated sulfides are associated with chimney and mound deposits found at the sites of ‘black smokers’, hydrothermal vents on the seafloor. The sulfides deposited at these sites have been concentrated by hot seawater percolating through the seafloor and being expelled onto the seabottom at the vents. When in contact with the cold ambient sea water, the hydrothermally heated water drops its mineral riches as sulfide-rich precipitates, forming the sulfide chimneys and mounds. The final authigenic mineral of economic interest is phosphorite, used primarily for phosphate fertilizer. The seabed phosphorites are found as nodules, crusts, irregular masses, pellets, and conglomerates on continental shelves and on the tops of seamounts and rises. Their distribution is widespread throughout the tropical and temperate oceans, although they are preferentially found in areas of oceanic upwelling and high organic productivity.

Whichever of these five mineral types is the target of a mining operation, following regional exploration the process of extracting the commodity of value has seven distinct steps. These steps are: (1) survey the mine site, (2) lease, (3) pick up the mineral, (4) lift and transport, (5) process, (6) refine and sell the metal, and (7) remediate the environmental damage. These steps will be considered in turn (**Figures 1–7**). Naturally, there are differences for each mineral type as well as a range of possible processes that can be used. While many of these processes have been tested and many are used in traditional terrestrial minerals operations, to date there is no commercially viable full-scale deep-sea authigenic mineral extraction operation.

## Survey

The first step in minerals development is to find an economic mine site. This is found by surveying and mineral sampling. A great deal of mineral sampling has already been done over the last 40 years throughout the world’s ocean. These data are available for initial planning purposes. Following a detailed literature review the prospective ocean miner would send out a research vessel to sample extensively in the areas under consideration. New acoustical techniques can be calibrated to show certain kinds of bottom cover, including the density of manganese nodule cover. This is one way to



**Figure 1** Generalized deep-sea mining system component diagram. This diagram illustrates the proposed collection and lift components which would apply to a wide variety of mineral systems. Note that a considerable variety of collector types are possible on the bottom, including tracked robotic miners, Archimedes screw-driven vehicles, or towed sleds. Both airlift and pumped systems are illustrated as possible lift mechanisms. (Reproduced with permission from Thiel *et al.*, 1998.)

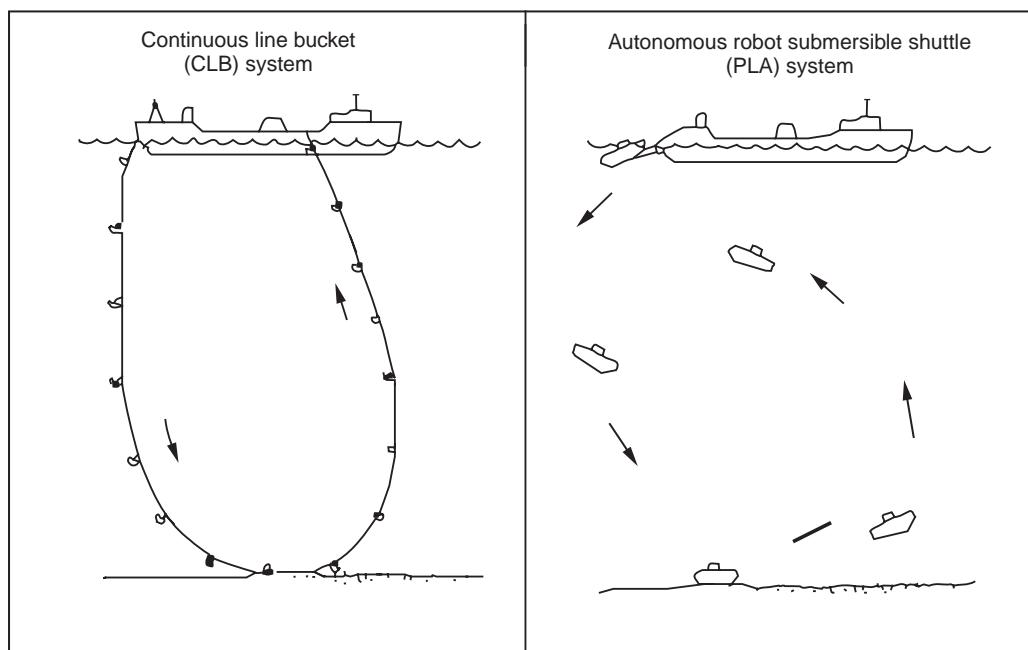
rapidly survey the bottom to highlight areas with potentially economic accumulation of authigenic minerals.

Significant advances in marine electronics, navigation, and autonomous underwater vehicles (AUVs) are being brought together. New ‘chirp’ sonars which transmit a long pulse of sound in which the frequency of the transmitted pulse changes linearly with time give high resolution and long-range seafloor and sub-bottom imagery. Navigation based on the satellite global positioning system (GPS) can now give accurate underwater positions ( $\leq 1$  m) when linked to an acoustic relay. This level of survey equipment is now available on underwater autonomous vehicles, meaning that the cost of a ship is not necessarily an impediment.

Sampling for metal concentrations follows the initial surveys. Sampling may be from a ship, a remotely operated vehicle (ROV), or a submersible. Sampling is likely to begin with dredges, progress to some kind of coring, and finish with carefully

oriented drilled samples giving a three-dimensional picture of the ore distribution. These data, after chemical analysis of the contained metals, will give grade and tonnage information. The grade and tonnage estimates of the deposit will be entered into a financial model to determine whether it is economically profitable to mine a given deposit.

In actual fact this process is iterative. A financial model will be used to indicate the type of mineral deposit which must be found. This will narrow the search area. As new data are forthcoming, increasing levels of survey sophistication will follow, assuming that the data continue to indicate an economic mining possibility. In its simplest form the financial model looks at sales of the metals derived from the mine, compared to the total cost of all the operations required to obtain the minerals and contained metals. If the projected sales are greater than the costs by an amount sufficient to allow a profit, typically on the order of a minimum of 20% after taxes, then the mineral deposit is economic. If not,



**Figure 2** In contrast to the more conventional marine mining systems illustrated in **Figure 1**, two other potential systems are the continuous line bucket system and the autonomous robot submersible shuttle. The continuous line bucket is a series of dredge buckets on a line dragged over the mineral deposit. The submersible shuttle system is a theoretical system using a series of robotic transport submersibles to carry ore from a collection point on the bottom to a waiting surface ship. (Reproduced with permission from Thiel *et al.*, 1998.)

costs must be decreased, sales increased or another more attractive deposit must be found. In the end, a deposit survey will be developed of sufficient detail to allow the production of a mining plan for the development of the property. Normally such a mining plan would need to be approved by the government authority granting mineral leases before actual mining could commence. At some point during the survey and evaluation process, the mining company needs to obtain a lease on the mineral claim in question. Usually this is done very early in the process, after the first broad area wide surveys.

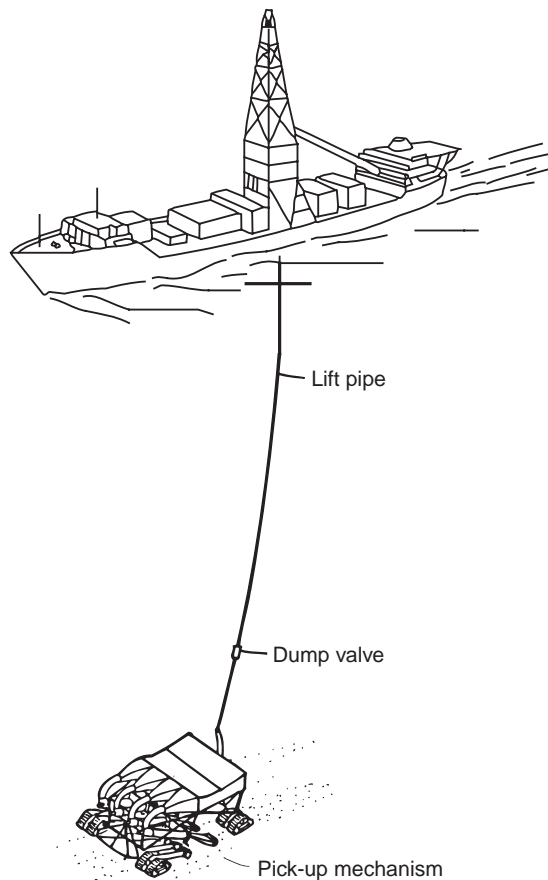
## Lease

Ocean floor minerals are not owned by a mining company. If the minerals are within the exclusive economic zone (EEZ) of a country, they are the property of that country's government. EEZs are normally 200 nautical miles off the coast of a given country, but in the case of a very broad continental shelf may be extended up to 350 miles offshore with recognition of the appropriate United Nations boundary commission. Beyond the EEZ, the ownership of minerals rests with the 'common heritage of mankind' and is administered for that purpose by

the United Nations International Seabed Authority in Kingston, Jamaica.

Both national regimes and the International Seabed Authority will lease seabed minerals to *bona fide* mining groups after the payment of fees and the arrangement for filing of mining and exploration plans, environmental impact statements, and remediation plans. The specific details of the requirements vary with the size of the proposed operation, the mineral sought, and the regime under which the application is made. In many countries, the offshore mining laws are modeled on the legislation which governs offshore oil development. This is not surprising as the issues are similar and worldwide the annual value of the offshore oil industry is in excess of \$100 billion, whereas the offshore mining industry will not be more than a few percent of this value for the foreseeable future.

Leasing arrangements vary from country to country. In the USA, offshore leasing of both hard minerals and oil and gas in the federally controlled waters of the EEZ (normally more than 3 miles offshore) falls under the Outer Continental Shelf Lands Act and is administered by the US Department of the Interior. This act requires a competitive lease sale of offshore tracts of land. The company to whom a lease is awarded is the one which offers the



**Figure 3** An engineering design for a proposed manganese crust mining system. (Reproduced with permission from State of Hawaii (1987). *Mining Development Scenario for Cobalt-Rich Manganese Crusts in the Exclusive Economic Zones of the Hawaiian Archipelago and Johnston Island*. Honolulu, Hawaii, Ocean Resources Branch.)

highest payment at a sealed bid auction. In addition to this payment, known as the bonus bid, there is also an annual per acre rental and a royalty payment which would be a percentage of the value of the mineral taken. A typical deep water rental for an oil and gas lease might be \$25 per acre per year with a royalty payment equal to 12.5% of the oil extracted. Hard mineral lease rentals and royalties could be expected to be lower, as the commodity is less valuable and the demand for access to offshore mineral resources is much less than for offshore oil.

### Mineral Pick Up

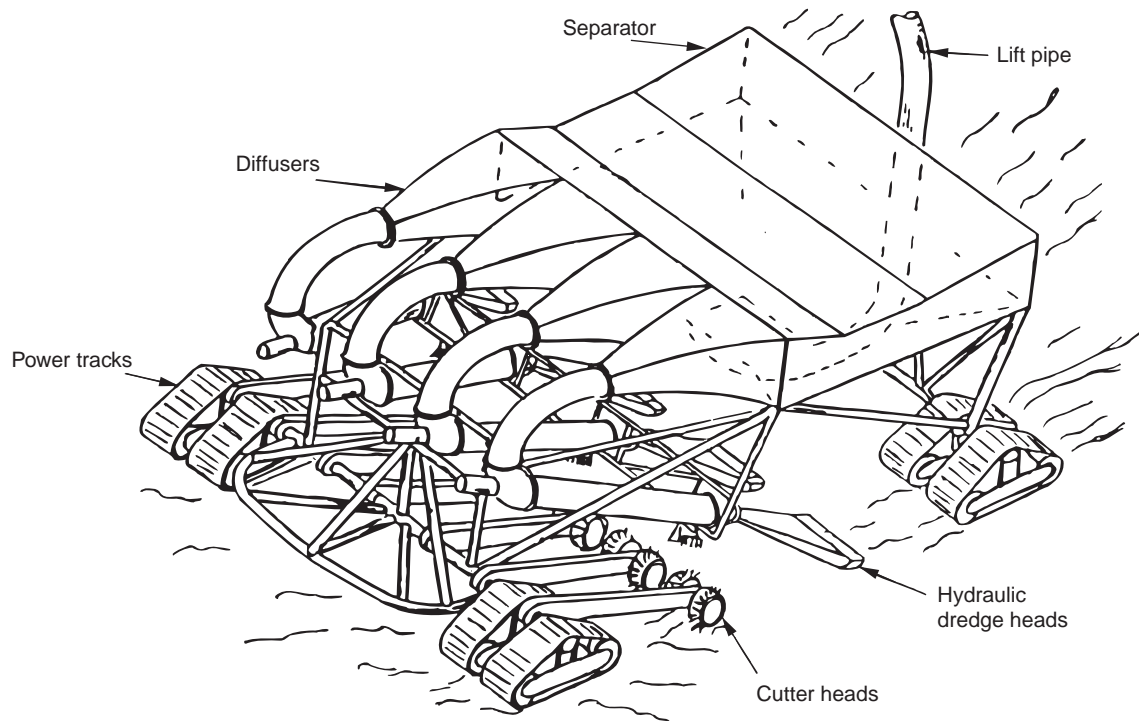
Once a deposit has been characterized and leased, a mining plan is drawn up. This plan will depend on the mineral to be mined. In general, several steps must be taken to mine. The first is separating the mineral from the bottom. In the case of polymetallic sulfide, manganese crust or underlying phosphorite,

a cutting operation is involved. In the case of phosphorite nodules, manganese nodules, or sulfide muds there is solely a pick-up operation. Cutting requires specialized cutting heads, often these are simply rotating drums with teeth (Figures 3–5). Such cutters have been developed for the dredging industry as well as the underground coal industry on land. The size, angle, and spacing of the teeth on a cutter are dependent on the rate of cutting desired and the size to which particles are to be broken. The overall mineral pickup rate is determined by the necessary rate of throughput at the mineral processing plant. This can be worked back to pick-up rate on the bottom. Engineering judgment then dictates whether this is best achieved with larger numbers of smaller cutters or a lower number of larger cutters. This may translate into multiple machines operating on the bottom and feeding one lift system.

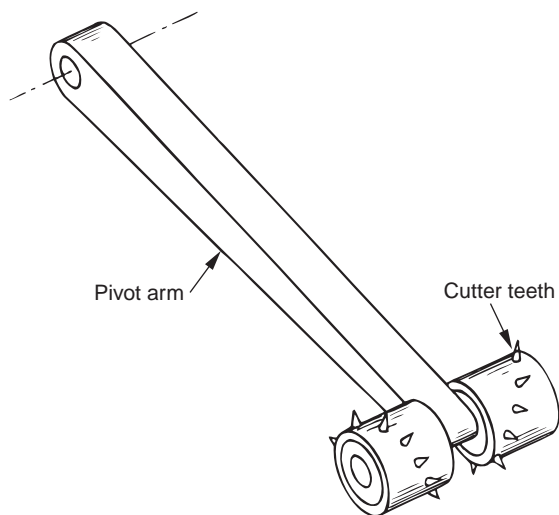
When the mineral is broken into sufficiently small pieces, these must then be collected for lifting. This is usually a scooping or vacuuming operation. Scooping is accomplished by blades of various shapes. Vacuuming is usually the result of a powerful airlift or pump farther up the line. One system tested by the Ocean Minerals Co. for picking up manganese nodules involved an Archimedes screw-driven robotic miner, which had two pontoons. A flange in screw-shaped spiral was welded onto each pontoon. The screws both served to drive the vehicle forward as well as pick up the nodules which were sitting in the mud it passed over. There may be a sieving or grinding step between mineral pick-up and lift. This serves two functions; the sieving gets rid of unwanted bottom sediment that may have become entrained in the ore; the grinding ensures that the particle size range going up the lift pipe is in the correct range to get optimum lift without clogging the pipe.

### Lift and Transport

Once the mineral has been cut off or picked up from the bottom it must be lifted to the surface. Over the years a number of systems have been suggested and tested for this purpose. The most successful of these tests have involved bringing the minerals to the surface in a seawater slurry in a steel pipe. This pipe would typically be 30–50 cm in diameter, hence it would be similar if not identical to pipe used in offshore oil drilling operations. Two methods have been tested for bringing the slurry up the pipe, i.e. pumps and airlift. Airlift is a commonly used technique in shallow-water dredging. Compressed air is introduced into the pipe, typically about a third of the way from the top (Figure 6). As the air expands



**Figure 4** A robotic miner designed to rip up and lift attached flat lying bottom deposits such as manganese crusts. (Reproduced with permission from State of Hawaii (1987) *Mining Development Scenario for Cobalt-Rich Manganese Crusts in the Exclusive Economic Zones of the Hawaiian Archipelago and Johnston Island*. Honolulu, Hawaii, Ocean Resources Branch.)

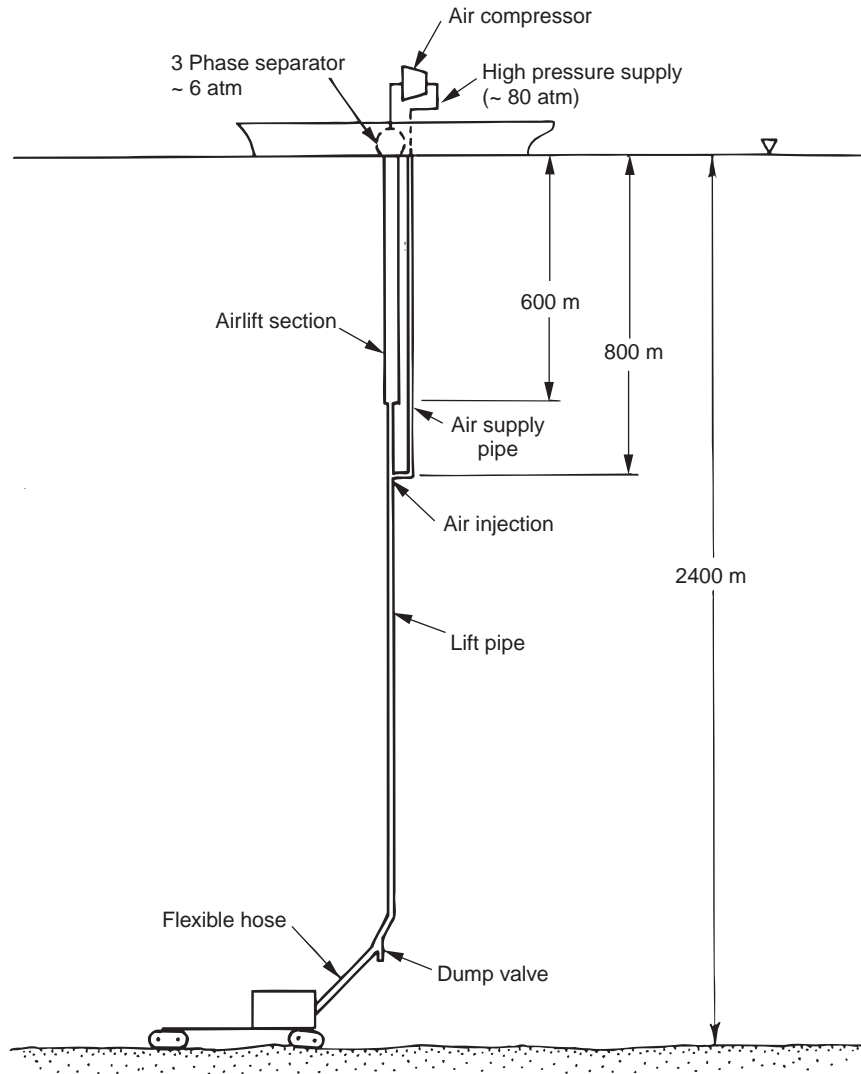


**Figure 5** Cutter head design for a bottom miner ripping attached ores such as polymetallic sulfides or manganese crusts. (Reproduced with permission from State of Hawaii (1987) *Mining Development Scenario for Cobalt-Rich Manganese Crusts in the Exclusive Economic Zones of the Hawaiian Archipelago and Johnston Island*. Honolulu, Hawaii, Ocean Resources Branch.)

moving upward in the pipe it draws the mineral slurry behind it. This works extremely well over lifts of a few hundred meters. It also works over lifts in

the deep sea of 6000 m, for example on manganese nodules, except that it is much more difficult to control. Hydraulically driven pump systems along the pipe's length have also been tested to full ocean depth. They also work and although easier to control may ultimately be less efficient lifting systems than an airlift.

Several other lift systems are possible (Figures 2–5). The most notable of these is the continuous line bucket, which is a series of buckets on a line which is continuously dragged over the mineral deposit. This system has been successfully tested, although it suffers the disadvantages of lack of control on the bottom, potentially wider spread environmental damage, and the possibility of the rope entangling on itself. A system proposed but not tested involves a series of ore-carrying robotic submersible shuttles. These shuttles would use waste mineral tailings as ballast to descend to the bottom, where they would exchange the ballast for a load of ore. Adjusting their buoyancy they would then rise to the surface, off-load the ore onto an ore carrier, reload waste, and return to the bottom. This is potentially a very elegant system in that it handles both tailings waste disposal and mineral lift at the same time, each with the expenditure of very little energy.

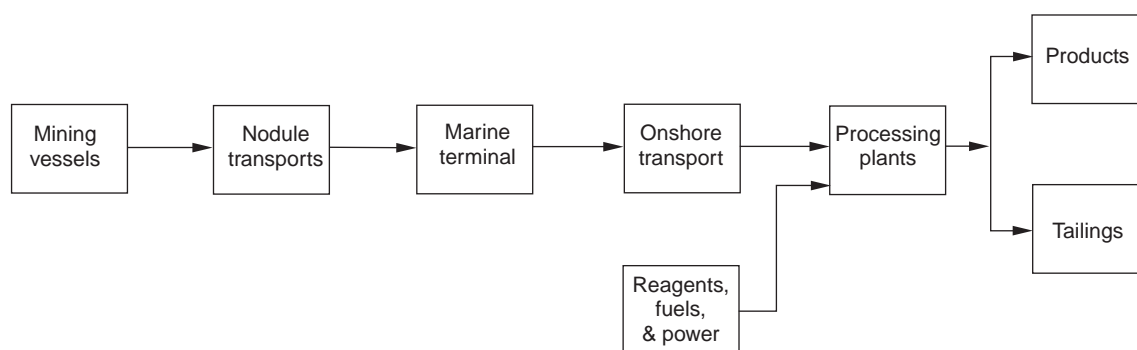


**Figure 6** Generalized design of an airlift system to lift ground minerals from the ocean bottom to the surface. (Reproduced with permission from State of Hawaii (1987) *Mining Development Scenario for Cobalt-Rich Manganese Crusts in the Exclusive Economic Zones of the Hawaiian Archipelago and Johnston Island*. Honolulu, Hawaii, Ocean Resources Branch.)

Once the ore is on the surface it must be taken to a processing plant. This processing plant can be an existing plant at a site on land, a purpose-built plant near a harbor to process marine minerals, a large offshore floating platform moored near the mine site on which a plant is built, or a ship converted to mineral processing. The latter two could be right at the mine site. The minerals would be processed as soon as they were lifted to the surface. For a shore-based processing plant a fleet of transport ships or barges would be required to move the lifted ore from the mine site to the plant. This could be a tug and barge operation or a series of dedicated ore carrier vessels.

## Processing

Once the minerals have been mined and transported to the processing location they must then be treated to remove the metals of interest. There are two basic ways to do this: smelting and leaching (pyrometallurgy and hydrometallurgy). Once a basic scenario of either reducing the mineral with acid or melting has been decided upon, there are a number of possible steps to partially separate out unwanted fractions of the mineral. In order to be economically viable, a mineral processing plant needs to process large tonnages of material. In the case of manganese nodules this might be 3 million tonnes  $y^{-1}$ . In order to process these large tonnages economically it is



**Figure 7** Components involved in a marine minerals extraction operation, each of which has an environmental effect and must be considered in the context of the whole operation. (Reproduced with permission from State of Hawaii (1981) *The Feasibility and Potential Impact of Manganese Nodule Processing in the Puna and Kohala Districts of Hawaii*. Honolulu, Hawaii, Ocean Resources Branch.)

important to separate out as much of the waste mineral material as early as possible in the process. This is done most commonly by magnetic separation, froth flotation, or a density separation such as heavy media separation. In an effort to make these processes more efficient the incoming ore would normally be washed to remove salt and ground to decrease the particle size and increase surface area.

Magnetic separation separates magnetic and paramagnetic fractions from nonmagnetic fractions. This technique can be done either wet or dry. Dry magnetic separation involves passing the ground ore through a strong magnetic field underlying a conveyor belt. The magnetic and paramagnetic fraction stay on the conveyor belt while the nonmagnetic fractions drop off as the belt goes over a descending roller. Manganese, cobalt, and nickel are paramagnetic, so this is a good separation technique for manganese nodules and crusts. Wet magnetic separation involves passing a slurry of ore over a series of magnetized steel balls. The magnetic and paramagnetic materials stick to the balls and the nonmagnetic fraction flows through. The level of separation depends on the strength of the magnetic field. Usually this is done with an electromagnet so that the field can be turned on and off.

Froth flotation relies on differences in the surface chemistry of the ore and waste grains. Sulfide ores in particular are more readily wet with oil than water. Grains of clay, sand, and other seabed detritus have the reverse tendency. Typically something like pine oil might be used to wet the mineral grains. The oil-wet ore is then introduced into a tank with an agent that produces bubbles, a commonly used chemical for this is sodium lauryl sulfate. The bubbles tend to stick to the oil-wet grains, which float them to the surface where they can be taken off in the froth at the top of the tank. The

waste material is allowed to settle in the tank and removed at the bottom. The separated ore is then washed to remove the chemicals. The chemicals are recycled if possible.

Another technique commonly used in mineral beneficiation is density separation. This can be as simple as panning for gold. In a simple panning operation or more complex sluice boxes or jigging tables, the heavy mineral (the gold) stays at the bottom, whereas the lighter waste materials are washed out in the swirling motion. A more sophisticated version of the same idea is to use a very dense liquid or colloidal suspension to allow less dense material to float on top and more dense material to sink. The density of the medium is adjusted to the density of the particular ore and waste to be separated. In general, heavy media suspensions, such as extremely finely ground ferro-silicon, are superior to traditional heavy liquids such as tetrabromoethane, which have a high toxicity.

Following mineral beneficiation, which removes the non-ore components, the ore itself must be broken down into its component value metals. Marine minerals can contain up to half a dozen economically desirable metals. In order to separate these metals individually, a reduction process must occur to break the chemical framework of the ore. This will either involve smelting or leaching. In a smelting operation the whole mineral structure is melted and the various metals are taken off in fractions of different densities which float on each other. Normally a series of fluxing agents is used. Clean separation in the case of a multi-metal ore can be a very exacting process. For highly complex polymetallic ores such as manganese nodules or crusts many experts favor a leaching approach over smelting in order to facilitate high purity separation of the metals. However, both leaching and smelting



processes have been tried on a variety of marine minerals and both types of process have been proved technically viable.

The most common leach agent is sulfuric acid as it is cheap, efficient, and readily available. Other acids, hydrogen peroxide, and even ammonia are also used as leaching agents. To reduce leaching times, temperature and pressure are raised in the leaching vessel. The leaching process breaks up the mineral structure and dissolves the contained metals into an acidic solution known as a 'pregnant liquor'. The metals become positive ions in solution. These individual metal ions must be separated out of the pregnant liquor and plated out as an elemental metal. This is done primarily in three processes: solvent extraction, ion exchange, and electrowinning. These may initially be done with the primary processing of the ore; however, the final phase of these techniques will be done in a dedicated metal refinery to achieve metal purity > 99%.

Solvent extraction relies on an organic solvent which is optimized to select one metal ion. This organic extractant is immiscible with the aqueous pregnant liquor. They are stirred together in a mixer forming an emulsion much like oil stirred into water. This emulsion has a very high contact area. The organic extractant takes the desired metal ion out of the aqueous phase and concentrates it in the organic phase. The aqueous and organic phases are then separated by density (usually the organic phase will float on the aqueous phase). The metal ion is then stripped out of the organic phase by an acidic solution and sent to an electrowinning step.

Instead of doing this extraction in a liquid as in the case of solvent extraction, it is possible to run the pregnant liquor over a series of ion-exchange beads in a column. The ionic beads have the property of collecting or releasing a given metallic ion, e.g. nickel, at a given pH. Therefore by adjusting the pH of the liquid flowing over the column it is possible to remove the nickel, for example, from the pregnant liquor, transferring it to its own tank, then remove copper or cobalt, etc. It is possible to use both solvent extraction and ion-exchange column steps in a particularly complex metal separation process or to achieve very high metal purities.

Following solvent extraction or ion exchange, the various metal ions have been separated from each other and each is in its own acidic solution. The standard concentration technique used to remove these metal ions from solution is electrowinning. The metal ions are positively charged in solution. They will be attracted to the negatively charged plate in a cell. A small current is set up between two or more plates in a tank. The positive metal ions

plate out on the negatively charged plate. Depending on the purity of the metal plated out and how strongly it is attached, either the metal is scraped off the plate and sold as powdered metal or the entire plate is sold as metal cathode, e.g. cathode cobalt.

## Refining and Metal Sales

Each of the metals produced by an offshore mining operation must be refined to meet highly exacting standards. The metals are sold on various exchanges in bulk lots. Silver, copper, nickel, lead, and zinc are largely sold on the London Metal Exchange. Platinum, silver, and gold are sold on the New York Mercantile Exchange. Both of these exchanges maintain informative internet websites with the current details and requirements for metals transactions ([www.lme.co.uk](http://www.lme.co.uk) and [www.nymex.com](http://www.nymex.com)). Cobalt, manganese and phosphate are sold through brokers or by direct contract between a mining company and end-users (e.g. a steel mill). Metal sales are by contract. The contracts specify the purity of the metal, its form (e.g. powder, pellets or 2 inch squares), the amount, place, and date that the metal must be delivered. Standard contracts allow for metal delivery as much as 27 months in the future (in the case of the London Metal Exchange). This allows a major futures market in metals and considerable speculation. This speculation allows metal producers to lock in a future price of which they are certain. In reality, only a few percent of the contracts written for future metal deliveries result in actual metal deliveries. The vast majority are traded among speculators over the time between the initial contract settlement and the metal delivery date. The price for a metal is highly dependent on its purity. Often metals are sold at several different grades. For example, cobalt is typically sold at a guaranteed purity of 99.8%. It may also be purchased at a discounted price for 99.3% purity and at a premium for 99.95%.

In order to achieve these grades considerable refining takes place. Often this is at a facility which is removed from the original mine site or processing plant. Metal refineries may be associated with the manufacturing of the final consumer endproduct. For example, a copper refinery will often take lower grade copper metal powder or even scrap and produce copper pipe, wire, cookware, or copper plate. Most modern metal fabricators rely on electric furnaces of some form to cast the final metal product. One of the techniques commonly used at refineries is known as 'zone refining' whereby a small segment of a piece of metal in a tube is progressively melted while progressing through a slowly moving electric

furnace coil. The impurities are driven forward in the liquid phase with the zone of melting. The purified metal resolidifies at the trailing edge of the melting zone. This technique has been used to reduce impurities to the parts per billion level.

### Remediation of the Mine Site

Once mining has taken place both the mine site and any processing site must be remediated (Figure 7). Considerable scientific work took place in the 1980s and 1990s looking at the rate that the ocean bottom recovers after being scraped in a mining operation. While it is clear that recovery does take place and is slow, it is still unclear how many years are involved. A period of several years to several decades appears likely for natural recolonization of an underwater mined site. It also appears that relatively little can be done to enhance this process. Once all mining equipment is removed from the site, nature is best left to her own processes.

An independent yet perhaps even more important issue is the way the waste products are handled after mineral processing. There are both liquid and solid wastes. The most advanced of a number of clean-up scenarios for the discharged liquids is to use some form of artificial ponds or wetlands, most often involving cattails (*Typha*) and peat moss (*Sphagnum*), the two species shown to be most adept at wastewater clean-up. Typically the wastewater will circulate over several limestone beds and through various artificial wetlands rich with these and related species. At the end of the circulation a certain amount of cleaned water is lost to ground water and the rest is usually sufficiently cleaned to dispose in a natural stream, lake, river, or ocean.

The larger and as yet less satisfactorily engineered problem is with solid waste. In fact, recent environmental work on manganese crusts has shown that 75% of the environmental problems associated with marine ferromanganese operations will be with the processing phase of the operation, particularly tailings disposal. Traditionally, mine tailings are dumped in a tailings pond and left. Current work

with manganese tailings has shown them to be a resource of considerable value in their own right. Tailings have applications in a range of building materials as well as in agriculture. Manganese tailings have been shown to be a useful additive as a fine-grained aggregate in concrete, to which they impart higher compressive strength, greater density, and reduced porosity. These tailings serve as an excellent filler for certain classes of resin-cast solid surfaces, tiles, asphalt, rubber, and plastics, as well as having applications in coatings and ceramics. Agricultural experiments extending over 2 years have documented that tailings mixed into the soil can significantly stimulate the growth of commercial hardwood trees and at least half a dozen other plant species. Finding beneficial uses for tailings is an important new direction in the sustainable environmental management of mineral waste.

### See also

**Authigenic Deposits. Hydrothermal Vent Deposits. Manganese Nodules. Mid-Ocean Ridge Geochemistry and Petrology. Remotely Operated Vehicles (ROVs).**

### Further Reading

- Cronan DS (1999) *Handbook of Marine Mineral Deposits*. Boca Raton: CRC Press.
- Cronan DS (1980) *Underwater Minerals*, London: Academic Press.
- Earney FCF (1990) *Marine Mineral Resources: Ocean Management and Policy*. London: Routledge.
- Glasby GP (ed.) (1977) *Marine Manganese Deposits*. Amsterdam: Elsevier.
- Nawab Z (1984) Red Sea mining: a new era. *Deep-Sea Research* 31A: 813–822.
- Thiel H, Angel M, Foell E, Rice A and Schriever G (1998) *Environmental Risks from Large-Scale Ecological Research in the Deep Sea – A Desk Study*. Luxembourg: European Commission, Office for Official Publications.
- Wiltshire J (2000) Marine Mineral Resources – State of Technology Report. *Marine Technology Society Journal* 34: no. 2, p. 56–59.

## MOLLUSKAN FISHERIES

**V. S. Kennedy**, University of Maryland, Cambridge, MD, USA

Copyright © 2001 Academic Press

doi:10.1006/rwos.2001.0454

### Introduction

The Phylum Mollusca, the second largest phylum in the animal kingdom with about 100 000 named species, includes commercially important gastropods,