MV Jaer bock 2003-4

Wetenschap

Can we dig it? by Prof. Ir. K.J. Weber

#### Introduction

The theme of this yearbook is the challenge to develop future resources that are at present outside our reach. We don't have to think of science fiction type ventures to other planets. On earth, 71 percent of the surface is covered by sea and so far we have only exploited some oil and gas fields, mostly in water depths of less than 250 m. In addition there has been some coastal mining of kassiterite, heavy minerals, gold and diamond. There are however three targets for future development that are of staggering size. Methane hydrates on the continental slopes may contain over  $2x10^{16}$  m<sup>3</sup> of methane. The deep ocean floors are covered by about  $1.5x10^{12}$  tons of manganese nodules in the Pacific alone. Finally there are the 40,000-mile long ocean ridges where new ocean floor is formed and massive sulfidic ore bodies are formed by black smokers. Looking at a map of the world the widespread distribution of the three targeted resources is remarkable (fig. 1).



Figure 1: Occurence of bottom-simulating reflections (BSR's) caused by methane hydrates, locations of hydrothermal mineral vents (HMV's) and areas where manganese nodules (MN's) are common.

Methane hydrates are currently very much in the picture and much exploration is carried out. Manganese nodules were a popular topic in the seventies but so far no economic venture has been undertaken. However the new developments in deep-sea technology may change this situation. Black smokers were only discovered in 1985 and brought about new insight into the genesis of several important metal ore bodies. Mining of the primary deposits may be possible but except for sampling of the vents no attempt has as yet been made. In the Red Sea hot metalliferous brines occur at 2000 m depth. A 3-months production test was carried out in 1979 with the drillship SEDCO 445 (Lück, 1982). It showed that pumping up the sediment from this depths was feasible but no commercial development followed.

### Methane hydrates

These hydrates were already encountered in 1930 in Siberia where they plugged pipelines, a phenomenon which is still an important problem especially in marine pipelines. However the prevalence of methane hydrates in the continental slopes and in permafrost areas was realised when seismic surveys showed reflections associated with the boundary between the hydrate zone and the free gas containing sediments underneath. These so-called bottom-simulating reflections (BSR's) have been observed in many places and formed the target for drilling expeditions by American, Japanese and Russian drillships.



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Figure 2: Lattice of hydrate crystal trapping methane molecule.

Tentatively the volume of methane in the hydrates is estimated to be two orders of magnitude larger than the conventional gas eserves  $(2.1 \times 10^{16} \text{ vs}, 2.5 \times 10^{14} \text{ m}^3)$ . Of this volume some  $10^{15} \text{ m}^3$  is in permafrost related hydrates on land (MacDonald, 1990).

With the fear of energy supply shortfalls in the not too distant future, it is logical that the methane hydrates are attracting much attention. Energy poor countries like Japan and India are interested but also the USA, Canada, Russia and Norway (Collett, 2002). There are already



Figure 3: Methane Hydrate stability curve with examples of hydrate zones in permafrost and continental slope settings.

a large number of papers on the subject and large sums of money are made available for research funding and drilling.

The gas hydrates are composed of pentagon dodecaeder shaped cages formed by 20 water molecules which can trap gas molecules like methane, ethane and propane (fig. 2). The hydrates are stable at a depth of about 100 m and a temperature of -10 °C in permafrost areas where the thickness of the stability zone depends on the depth to which the permafrost reaches and the geothermal gradient underneath. The hydrate stability curve (fig. 3) shows that in the continental slope sediments for a water depth of 100 m, a sea bottom temperature of 2°C and a geothermal gradient of 3°C per 100 m, a BSR can be expected at a depth of 1550-1600 m subsea. BSR's have been observed

in water depths of 500-4000 m and a depth of 100-1100 m below the seafloor. Pressurized core show the hydrates in the sediments looking like ice which however can burn. Depending on the degree of methane trapping, a cubic meter of hydrate can release 150-180 m<sup>3</sup> of methane.

The major drilling campaigns, so far, have been carried out by the drillship 'JOIDES Revolution'. This program will be continued, managed by the Joint Oceanographic Institution (JOI), a Washington based consortium of 18 public institutions. In September 2003, the JOI won a 10-year \$625 million contract as the US contribution to the international drilling projects. More money is funded by the other member states.

Japan drilled wells in the Nankai Trough methane hydrate area. A new very powerful drilling vessel, the Chikyu, has just been completed and will start operating in 2004. Japan National Oil Company and the Geological Survey of Canada are leading a consortium which drilled wells at the Malik site in the Mackenzie Delta in Northern Canada. Gas was produced from hydrates and the result will be used to model the potential of other areas (Dallimore et al., 1999).

In the USA the gas hydrate research is coordinated by the Department of Energy (DOE) together with the USGS. In Alaska a well was spudded by Anadarko in 2003. The Alaska gas hydrates form a major target for a joint BP/DOE research project to test gas hydrate production and also estimate the volume of gas trapped underneath the hydrate zone. The hydrate related methane alone is estimated at about  $10^{12}$  m<sup>3</sup> in the Prudhoe Bay-Kuparuk River area (Collett, 2002).



Figure 4: Optimal conditions for methane hydrate exploitation on continental slopes.

In Russia it is thought that methane has been recovered from hydrates following the pressure decline resulting from producing underlying free gas in the Messoyakha field in Western Siberia, discovered in 1968 (Collet et al., 1998). This process of dissociating the hydrates through pressure reduction appears the most economic way of liberating the trapped methane.

The biggest problem associated with most oceanic methane hydrate deposits is the mode of occurrence as dessimated nodules, veins, laminae and cements in low permeable unconsolidated very fine-grained sediments. Although one can compute volumes of  $0.5-1.5 \ge 10^9$  m<sup>3</sup> of methane per km<sup>2</sup> in several hundred meter thick zones, effective extraction is highly problematic. However the hydrates also occur in reservoir quality sandstones, as is the case in Alaska and Siberia. Obviously the challenge is to locate hydrate bearing large sandstone bodies on continental slopes. In the Gulf of Mexico and in the Nankai Trough such sandstone reservoirs have been discovered.

The research that would be very suitable for carrying out in Delft consists of sedimentological studies of deep-sea turbidite deposits, which form the major sandstone bodies in the hydrate prone areas. Sophisticated seismic analysis of such formations using new methods such as deep-towed multichannel streamers would be a great help in making detailed calibrated reservoir models (Breitzke et al, 2003). Studies on recovery methods based on those realistic models can follow to determine optimal development strategies. It is clearly the right time to get involved in the international consortia to reap full benefits of the mass of data that will be forthcoming in the near future and the generous funding of hydrate related research.

## Manganese Nodules



The occurrence of manganese nodules has been known since the first deep-sea dredging expeditions in the middle of the 19th century. In 1872 the 'Challenger' expedition dredged up nodules from the abyssal plain to the southwest of the island of Juan Fernandez in the Pacific (fig. 5). Since that time vast fields of these nodules have been observed and sampled almost everywhere where we find flat ocean floors covered by so-called red clays at a depth of over 4000 m, characterized by very slow sedimentation ( $\approx 1 \text{ mm}/1000 \text{ years}$ ). The sea bottom consists of reddish to brown sediments consisting of wind-

Figure 5: Cross-section of a manganese nodule formed around the ear bone of a cetacean, Mesoplodon, dredged from 2600 fathoms during the Challenger expedition in 1872, to the SW of the island of Juan Fernandez in the Pacific Ocean.

born clay, volcanic ashes, some meteoric particles and rock waste from icebergs. In addition, because of the slow sedimentation rate, resistant skeletal parts, like shark teeth and ear bones of whales are relatively common. They often form the nucleus of the nodules, covered by onion-like layers of manganese and iron oxides.

The total area of the red clay covered ocean floor with an average depth of about 4500 m is  $130 \times 10^6 \text{ km}^2$  (fig. 1). The most prolific areas are in the Pacific while the nodules in the Atlantic and Indian Ocean are somewhat less densely distributed and of a lower metal grade (Blissenbach 1974). In the best areas some more systematic sampling was carried out resulting in the range of metal content shown in table 1. Sometimes there are 5 kg of nodules per square meter and a maximum of  $10^4 \text{ tons/km}^2$  is also mentioned.

	Maximum percentage	Minimum percentage	Average percentage
Manganese	41.1	8.2	24
Iron	26.6	2.4	12
Cobalt	2.3	0.014	0.5
Nickel	2.0	0.16	1.0
Copper	1.6	0.028	0.5

Table 1: Range of metal content in 54 samples from the Pacific.

Preussag AG of Hannover conducted exploration in the Pacific east and south of Hawaii in 1972-1973 with the research vessel FS 'Valdivia', (Fellerer 1973). They determined that a mining project producing 3 million tons of nodules would require a 25,000 to 50,000 km<sup>2</sup> concession area over a period of 15 years. This means that the seafloor gathering system must be capable of harvesting the nodules over 5 to 9 km<sup>2</sup> which appears quite a tall order. In figures showing tentative development schemes (Gans 1986) one sees vehicles with gathering systems driving across the ocean floor (fig. 6). Imagine such a vehicle with a 10 m wide nodule remover, moving at a speed of 20 m/minute, which is a high estimate. This machine would only harvest over less than 1/3 of a square kilometre per day. Obviously novel methods have to be developed to gather the nodules.

In Delft ocean marine mining was introduced as a study subject in 1970, on the initiative of prof. Velzeboer. In 1975 M.G. A-Tjak became professor in marine mining (A-Tjak, 1975). Manganese nodules were one of the research subjects. Because much of the manganese production takes place in Russia, there was interest in the west to develop own sources of this metal during these cold war days.

In 1974 it appeared that an effort was going to be made to test commercial production of the nodules by the 'Glomar Explorer' a special ship, officially owned by the mysterious millionaire Howard Hughes. However in reality this vessel was designed and financed by the CIA with the purpose to salvage the Russian submarine K-129. This was a Golf II-type submarine, which



Figure 6: Design for the production of manganese nodules (from Gans, 1986).

accidentally sank in the Pacific in 1968 with several nuclear missiles on board. The salvage from a depth of about 5000 m was remarkable but in the end unsuccessful because the wreck disintegrated and only a small part was raised with some bodies but no missiles or codebooks.

Even Shell got involved in the manganese nodules when the Billiton Company, then owned by Shell, joined an American-Dutch consortium together with Lockheed, AMOCO and Boskalis. By 1988 this consortium, the "Ocean Minerals Company" had invested about 100 million dollars in deep-sea mining and exploration and research.

Interest in the nodules declined when it became clear that extracting the various metals from the ore was a costly process requiring very large investments.

Another complication was the large variation in metal content (table 1) which makes economic planning difficult without intensive sampling. Fluctuations of the metal prices also makes this planning hazardous. The decline of these prices during the economic recession in 1988 was the signal for Billiton to reduce their activities in the deap-sea research.

With respect to the jurisdiction over the deep-sea minerals in the international area, the United Nations accepted the principle that these resources form the common heritage of mankind. After long negotiations the Third Conference on the Law-of-the-Sea ended in 1982 with the signing of the "Convention on the Law-of-the-Sea" by 117 countries (Taverne, 1982). Problems were the objections by particularly the USA against a too large influence of

the developing nations and the requirements for the transfer of technology. The countries producing manganese, nickel and cobalt feared that the production of large quantities of manganese nodules would lead to serious competition on the world market.

The Convention puts the control of the deep-sea exploitation in the hands of the "Sea-Bed Authority" composed of representatives of UN member states. The "Enterprise" is the operational branch of the Sea-Bed-Authority. The Convention prescribes the allotment of concessions, taxation, transfer of technology and production restrictions (Taverne, 1993). On 16 November 1994 the Convention became effective after the ratification by 60 countries. Although the Convention principally deals with manganese nodules, other resources in the international area are also subject to the new laws although this will mean the addition of specific regulations for hydrates or black smokers.

It remains to be seen how this Convention will work out in practice when a mining project will be proposed. The nodules are theoretically a vast resource of metals. In the Pacific there may be in total some 250 billion tons of manganese and about 10 billion tons of copper, nickel and cobalt.

Looking at the fast progress in deep-sea apparatus in the oil industry it is likely that practical deep-sea mining techniques can be developed. Risers of kilometres long are already in use. Electrical cables to great depth, remotely controlled robots and automatic positioning are all possible. When unmanned vehicles can be steered on Mars, it must also be possible to drive unmanned harvesters over the seafloors.

In Delft research may be carried out to see what oil industry techniques might be developed for mining purposes. Also it would be interesting to think of methods to transport nodules to a central point by pumping. Raising the nodule material to the surface is another research topic. A possibility might be to mill the nodules to sand size and float them to the surface in an emulsion lighter than seawater. The chemical treatment of the ore would also be a most useful subject but unfortunately this type of research is no longer carried out in the faculty.

## Black smokers and their associated ore bodies

In the yearbook of 1995-1996, prof. Van Leeuwen wrote a paper on mineral resources of the future with the subtitle: 'The case of the volcanogenic massive sulfide deposits' (VMSD's). After the discovery of hot metalliferous brines in the deeper parts along the axis of the Red Sea in the sixties, there followed a period of geophysical investigations of the mid-ocean ridges with towed arrays. However the construction of the deep diving mini-sub 'Alvin' allowed the direct inspection of the axial zone of a ridge in the early nineties. The process of seafloor spreading with red hot lava extruding from the rift could be directly observed.

Sensational was the discovery of the black smokers (fig. 7) and their associated assembly of sulfer eating bacteria, tube worms, sea stars, shrimps and giant clams. Low-salinity, gas rich vapours are blown out through vents as a white plume, which quickly turns grey a few centimetres above the orifice. The temperature of this fluid is about 350 °C but the surrounding cold seawater causes sublimation of sulfides around the vents. This is thought to be the mechanism of the formation of the massive sulfide deposits, which are known from for example the Hokuroko district in Japan, the Noranda mining district in Canada and the Oman Mountains copper mines.

Because of the dynamic situation along the axial zones, an area with vents will be destroyed and buried under fresh pillow lavas. However from the mined deposits we can conclude that large lenses of sulfidic ores can be formed. Some of the older, still active vent areas may be surrounded by such lenses. Although the composition of the vented fluids varies considerably, they are often rich in Cu, Cd, Pb, Zn, Ag and Au. The composition of the ores can



Figure 7: Black smokers in the axial zone of the mid-ocean ridges where new seafloor is formed of pillow basalts. Seawater mixes with hydrothermal fluids and the hot sulferous brines rise to the seafloor via fractures.

be studied at the surface in for example the copper mines in the Oman Al-Hajar Mountains where pillow lavas contain sulfide ores. It is interesting that the obducted ophiolite package overlies another marine deep-sea formation, which contains manganese nodules.

Direct mining of the sulfidic ores in the black smoker zones is not yet planned, however there is no reason why areas of vents, where the hydrothermal activity has died down, could not be mined without causing major outbursts of fluids. Thus it is interesting to do research on methods to disintegrate and lift ore material from these very accidented vent areas from a depth of about 2500 m. Tests would be required to measure the strength of the vent material and the composition of these primary ores. In Delft one could start with a thorough investigation of all ophiolite related massive sulfidic ore bodies. Pleasant places like the Trodus Mountains on Cyprus suggest themselves.

## Conclusions

The three resources, which have been discussed, cover a large part of the Earth's surface. Nevertheless it is clear that economic recovery is very difficult. The methane hydrates occurring in reservoir quality sandstone with underlying free gas may be a suitable target and merit research efforts.

To successfully recover manganese nodules is mainly a technical problem but with the ongoing progress in deep-sea technology may be feasible in the future.

Finally, the black smokers form an interesting study subject both from a theoretical point of view as ore formers as well as a possible source of recoverable metals.

The question: '*Can you dig it?*' forms a major challenge with respect to the above resources and begs for a well designed research programme very suitable for Applied Earth Sciences students.

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