

**A CRITIQUE OF JAPANESE  
ACID MINE DRAINAGE  
TECHNOLOGY**

**MEND Report 6.3**

This report results from solicitation of proposals in 1992 by the New Ideas Task Force of the Mine Environment Neutral Drainage (MEND) Program.

The views and technical recommendations in this report are those of the author and do not necessarily reflect those of MEND.

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**A Critique of Japanese Acid Mine Drainage Technology**

**by**

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## EXECUTIVE SUMMARY

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This report was written following a two-week reconnaissance trip to Japan in late May and early June of 1993 by the author. Visits were made to a cross-section of government, industrial and university laboratories and research institutes engaged in acid-mine drainage studies. Introductions and appointments had been arranged in advance by a Japanese colleague and researcher in the field.

Most of the groups visited had been actively involved in this kind of research for the past two decades. There was found to be a high degree of collaboration and unanimity of purpose between the various sectors involved in the research to the extent that one could almost consider it an integrated national effort. This is surprising, considering that there is now very little mining carried out in Japan, although the smelting of imported ores and concentrates continues to be a major industry. There appeared to be a consensus that the development of new treatment technologies will form the basis of a lucrative new industry both nationally and internationally. In addition, it is accepted that to protect those of its mineral supplies originating in developing countries, Japan must assist these countries in all aspects of mineral exploitation, including environmental protection measures.

Some new technologies have been fully developed and successfully introduced, notably those based on the bacterial oxidation of ferrous iron, such as the Matsuo Mine acid drainage treatment plant, the Dowa Mining Company's flue-gas de-sulphurization system, the flue-dust treatment system in operation at the Dowa Mining Kosaka smelter and the recovery of marketable ferric sulphate solution at the Kosaka smelter. The Ferrite and Iron Powder processes developed at two Tokyo universities are also now widely used in Japan for the treatment of metalliferous industrial effluents. The sludge-densification process based on re-cycling precipitated sludge particles from the settling tank back to the neutralizing tank, is being successfully operated in several plants.

Other new technologies have been extensively developed, but not yet introduced. These include systems for the recovery of ferrite and hematite from iron-rich mine drainage waters and a flotation process for the recovery of a range of metals from mine drainage waters.

At the present time, a whole range of new technological approaches is being examined, but are in the early or middle stages of development. The most important of these are processes involving ion-exchange technology, membrane technology, sulphate-reducing bacteria, sulphur-oxidizing bacteria and metal-absorbing organisms. Also, plans to use the stopes in abandoned mines for the disposal of sludges and solid wastes are being seriously investigated.

The main recommendation of the report is that the setting-up of a new research fund specifically designated for joint Canada-Japan collaboration in the field of acid mine drainage be explored. Financing of this new funding source to be shared by the Mine Environment Neutral Drainage (MEND) program and the Metal Mining Agency of Japan (MMAJ).

Le présent rapport fait suite à une visite de deux semaines que nous avons faite au Japon à la fin de mai et au début de juin 1993. Nous nous sommes rendus dans divers laboratoires du gouvernement, de l'industrie, des universités et des instituts de recherche où on mène des études sur le drainage minier acide. Un collègue japonais dont les recherches portent sur ce sujet avait préparé notre séjour en fixant des rendez-vous et en organisant des rencontres.

La plupart des groupes que nous avons rencontrés mènent des recherches dans ce domaine depuis une vingtaine d'années. Nous avons constaté que les divers secteurs qui participent à ces travaux collaborent étroitement les uns avec les autres et partagent les mêmes objectifs, de sorte qu'on pourrait presque parler d'un effort structuré à l'échelle nationale. L'ampleur de ces travaux est étonnante si l'on considère que le Japon exploite actuellement très peu de mines, bien que la fusion de minerais et de concentrés importés demeure une industrie importante. On semble cependant s'entendre sur le fait que le développement de nouvelles technologies de traitement permettra de créer à l'échelle nationale et internationale une nouvelle industrie très lucrative. On reconnaît de plus que si le Japon veut conserver l'accès aux ressources minérales des pays en voie de développement, il devra aider ces pays dans tous les aspects de l'exploitation minière, y compris les mesures de protection de l'environnement.

Un certain nombre de nouvelles technologies ont été mises au point et appliquées avec succès, notamment les procédés fondés sur l'oxydation bactérienne du fer ferreux, comme ceux qu'on utilise à l'usine de traitement du drainage acide de la Matsuo Mine, le système de désulfuration des gaz de combustion de la Dowa Mining Company ainsi que le système de traitement des poussières et le procédé de récupération de solutions commercialisables de sulfate ferrique utilisés à la fonderie de Kosaka de la Dowa Mining. L'utilisation des procédés de traitement des effluents industriels métallifères par ferrites et poudre de fer développés dans deux universités de Tokyo est maintenant très répandue au Japon. On exploite dans plusieurs usines un procédé de densification des boues par recirculation dans un bassin de neutralisation des précipités formés dans le décanteur.

D'autres technologies ont été mises au point mais n'ont pas encore été appliquées, notamment des systèmes de récupération des ferrites et de l'hématite présents dans les eaux de drainage à haute teneur en fer et un procédé de flottation pour la récupération de divers métaux présents dans les eaux de drainage minier acides.

Toute une gamme de nouvelles méthodes sont actuellement à l'étude, mais les travaux de développement en sont encore aux premiers stades. Les plus importantes de ces méthodes utilisent des techniques d'échange d'ions, des techniques de membrane, des bactéries sulfatoréductrices, des bactéries oxydantes du soufre et des organismes capables d'absorber les métaux. On étudie en outre sérieusement la possibilité d'utiliser les chambres de mines abandonnées pour l'enfouissement des boues et des déchets solides.

La conclusion principale du rapport est qu'on devrait envisager la création d'un fonds de recherche réservée aux collaborations entre le Canada et le Japon dans le domaine du drainage minier acide. Le Programme de neutralisation des eaux de drainage dans l'environnement minier (NEDEM) et la Metal Mining Agency of Japan se partageraient les frais de cette nouvelle source financière.

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## **2 INTRODUCTION**

### **2.1 Background**

Japan has a long history in mining and metallurgy, and although mining activity in Japan itself has now almost come to an end, Japanese mining companies are extensively involved in joint ventures with other countries, and so continue with their mining operations overseas. Also, the smelting and concentration in Japan of ores purchased overseas continues. These realities alone provide a rationale for the great interest shown by the Japanese government and by Japanese companies in mine-waste treatment in recent years. But there are perceived to be additional reasons for pursuing research in this area. Much of the technology for mine-waste treatment is also applicable to the hydrometallurgical extraction of metals. This is regarded as being a technological field with a very promising future. In addition, the Japanese seem to be very conscious of the fact that environmental awareness is growing all over the world, and that the market for waste-treatment facilities of all types will continue to grow, and that sound treatment technology is a marketable product. The author was impressed by the large numbers of university, government and private sector research groups working in this field. Most Japanese university science and engineering departments treat their waste-water with in-house treatment facilities before discharge into the municipal sewage system. It seems that no Canadian university has such a treatment plant in operation. The situation in Japan is relevant to Canada because they find themselves now in the situation we will be in, in a few years. Government restrictions will become ever more severe, and companies and institutions will be forced to confront environmental problems that can at present be ignored. The extent of research and development into practical ways of dealing with real-world environmental problems is most impressive.

### **2.2 Environmental awareness in Japan**

For thousands of years, the Japanese people enjoyed a remarkably clean environment, because the climate is windy and wet, and the winds tend to blow away air pollution while the heavy spring rains flush out river-borne pollutants to the sea. However, the growth of heavy industry since the Meiji revolution (1868) led to a deterioration in air and water quality and to several serious pollution incidents involving the death or disablement of thousands of people. The most well-known of these incidents being :

- Copper and arsenic pollution of the Watarase river by effluent from the Ashio mine caused more than 1000 deaths from consuming poisoned agricultural products (~1890).
- Methylmercury pollution in fish in Minamata Bay caused the first outbreak of "Minamata disease" (~1953).
- Cadmium pollution in rice from fields near the Kamioka mine caused outbreaks of "Itai-itai disease" (~1960).
- Methylmercury pollution in fish in the Agano river caused a second outbreak of "Minamata disease" (~1964).

In the beginning, companies were able to give cash settlements to the rural poor effected by the toxic effluents and thereby avoid making serious efforts to prevent pollution. This situation eventually changed when the first lawsuit by victims of pollution against the company responsible began in 1964. This lawsuit was successful, and some Minamata disease victims were awarded damages in 1973 - others have only very recently been compensated. Removal of mercury-polluted mud from Minamata Bay began in 1983. After a long struggle by Japanese environmentalists, anti-pollution regulations in Japan are now quite stringent and public opinion is strongly in favour of strict enforcement. Most companies now take environmental concerns very seriously, and there appears to be a general consensus that it makes good economic sense for government, industry and the universities to work together to find new technologies to combat this problem.

### **2.3 Organization of the Japanese Mining and Metals Industry**

The responsibility for minerals policy in Japan rests ultimately with the Ministry for International Trade and Industry (MITI). This ministry has a variety of subsidiary agencies and departments, each responsible for certain aspects of this policy, but with some overlap between the various divisions. The most important agencies from the point of view of the mining industry are : i) The Agency of Industrial Science and Technology (AIST) and ii) The Metal Mining Agency of Japan (MMAJ). AIST is responsible for the administration of the Geological Survey of Japan, and sixteen research institutes, seven of which are regional and nine central. Many of these institutes are engaged in research relating to the treatment of acid mine drainage. A new organisation - the Eco-Mining Centre - is of particular interest, since it is destined to play a central role in the financing of mine drainage treatment in the future. A description of this new Centre is given in section 2.4 of this report.

The organization chart on Figure 1 illustrates the general relationships between the different agencies and divisions.

### **2.4 The Centre for Eco-Mining**

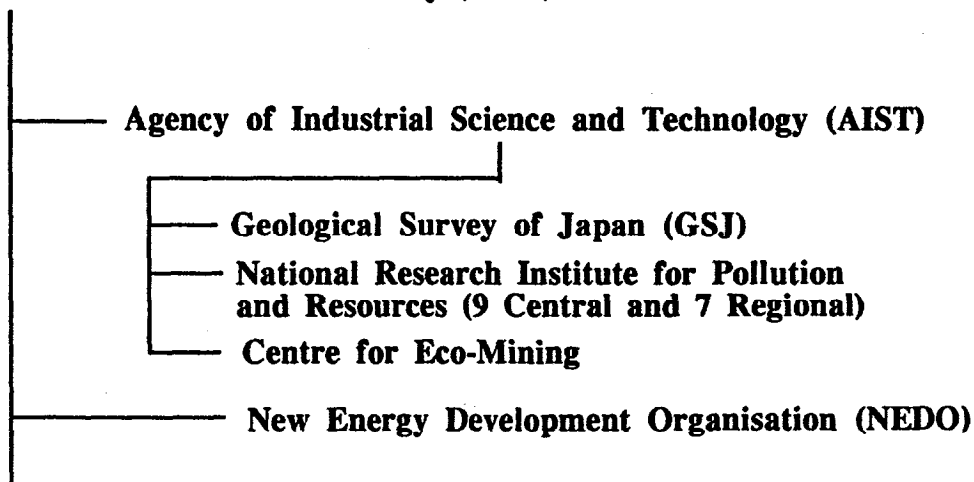
In Japan the principle has been established that mining companies are responsible for the environmental effects of their operations even after mining has ceased. Mining companies are naturally concerned that the costs of keeping a treatment plant running at an abandoned mine-site could continue for the foreseeable future. This problem has been addressed, and the compromise solution reached involves some government assistance, but the mining companies pay the estimated cost of maintaining a clean environment in the vicinity of their sites for twenty years after shutdown. The scheme is administered by a new organisation called the Centre for Eco-Mining. This is a non-profit organisation set up in December 1992 and financed by 17 mining companies. Additional financial support is provided by MITI. Among the activities involving the centre are : mine reclamation and research and development in environmental protection. Once a mine becomes closed, the company concerned will pay the twenty-year treatment costs over a six-year period. All this money will be pooled and invested. The interest on the capital will be used for the building and operating costs of the treatment plants, in perpetuity. It appears that the scheme calls for the government to make up any shortfall in the fund.



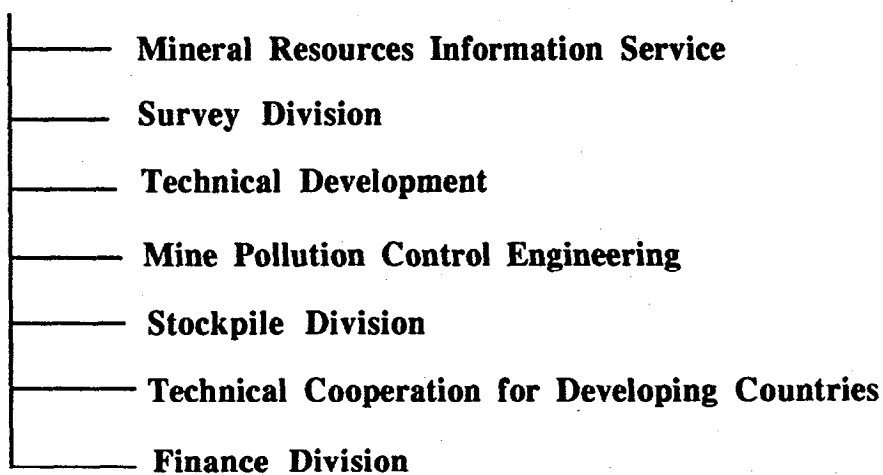
The Technical Head of the new centre is Mr Kinzo YASUDA who has been recruited from the private sector.

Figure 1. Organizational chart for the mining/metals industry of Japan

**Ministry of International Trade and Industry (MITI)**



**Metal Mining Agency of Japan (MMAJ)**



### **3 REPORT OF VISIT**

#### **3.1 Introduction**

The author travelled in Japan for a two-week period from May 25th -June 8th, 1993. During this time, he visited several government research laboratories, two private sector research institutes, a mine-site and a total of seven research groups in different universities. A brief summary of the people interviewed, and their interests, follows. Detailed accounts of the most interesting research projects are given later.

#### **3.2 Sendai - The Government Industrial Research Institute Tohoku (GIRIT)**

This is one of the seven regional and nine central research institutes belonging to the Agency for Industrial Science and Technology (AIST), which is under the Ministry of International Trade and Industry (MITI). GIRIT was established in 1967 with the aim of developing the industrial technology of the Tohoku region. The busy industrial city of Sendai, with a population of almost one million, lies about 330 km north of Tokyo. It is anticipated that Sendai will become the second centre, after Tokyo, of advanced technology in materials science and metal composites. GIRIT has a staff of 54, of whom some 40 are laboratory researchers. Most of the research projects are carried out with industrial collaboration, and funding is provided by MITI, other government agencies and industry. The Chemistry Department appeared well-equipped for metals analyses, having a Hitachi AA and a Seiko ICP, both nearly new, as well as many other instruments. During the visit, meetings were held with the Head of Research, Toyoaki OKADA, the Head of Research Planning, Dr Toshishige SUZUKI and a research chemist, Katsuyoshi MORI. Dr Suzuki is involved in the development of new ion-exchange resins for separating precious metals and fluoride from industrial effluents [1, 2]. Mr Mori has worked on the development of an ion-flotation process for the recovery of metals from mine waste waters [3 - 7].

#### **3.3 Morioka - Iwate University**

The quiet city of Morioka, which lies some 450 km north of Tokyo has a population of about 130,000. It is situated near the mountains, and is a well-known winter-sports centre. Iwate University is a small state university with about 1,200 students. the author visited the Faculty of Engineering, as the guest of Dr Tatsuo OMURA (a professor in the Department of Civil and Environmental Engineering) and Dr Hiroshi NAKAZAWA (an associate professor in the Department of Mineral Development Engineering). Dr Omura is involved in a variety of environmental engineering projects, including a study of iron-oxidising bacteria held on different support media, and also a study of the inhibitory effects of different metal ions on the iron-oxidising capabilities of these bacteria [8 - 10]. Dr Nakazawa collaborates with Dr Omura in a project to extract heavy metals from sewage sludge.

### **3.4 Matsuo - The Matsuo Mine**

The Matsuo mine is an abandoned sulphur (pyrite) mine located at the edge of a national park about 60 km north-west of Morioka City. The mine closed down some twenty years ago, due to the availability of cheap sulphur from petrochemical plants. Acid drainage from the mine, containing very high levels of iron, drained into the Kitakami river, which became stained a deep rusty-red colour. In order to eliminate this problem, the drainage from the site was reduced by plugging some of the lower mine galleries, diverting rainfall and spring melt runoff through tunnels and planting vegetation over the whole site. In addition, a water-treatment plant incorporating a bacterial oxidation step was constructed. This plant has now been operating successfully for over ten years, under the direction of the Metal Mining Agency of Japan [11, 12]. The Deputy Director of the operation, Mr Takeshi HATAKEYAMA, was kind enough to show the author around the whole facility.

### **3.5 Tokyo - The Metal Mining Agency of Japan (MMAJ)**

During his visit to MMAJ, the author met with Hideo SETOYA, the Director General of the Technical Development Department, Kenji SAWADA, the Director of the Technical Development Department, Eiji KUBOKI, the Deputy Director of the Technical Development Department and Eitarou HASHIMOTO, the Senior Mineral Processing Engineer of the Technical Development Department. The Metal Mining Agency of Japan is a sub-agency of MITI, with the overall responsibility of securing Japan's supplies of metals and metal ores, and maintaining the stockpiles of strategic metals. It has 12 overseas offices, including one in Vancouver, to coordinate contracts for metal and ore purchases and to help initiate joint ventures, especially in developing countries. MMAJ maintains a world-wide data-base on mineral resources, for which information is continually being collected. The agency is also heavily involved in mineral exploration all over the world, both on land and at sea. Their budget for exploration is some US\$100 million annually. MMAJ is also involved in technology assistance and technology transfer to developing countries, with the aim of assuring long-term supplies of metals for Japanese industry. The agency carries out extensive research and development in the area of pollution control related to mining and smelting.

### **3.6 Tokyo - The Shimizu Corporation Institute of Technology (Advanced Technology Research Department)**

The Shimizu Corporation, which has been in operation for some 180 years, is one of the world's largest construction companies, with 91 offices and subsidiaries in 33 countries. The Institute of Technology was formed in 1944 with the objective of developing and adapting new technologies to keep the company at the forefront of innovation in the construction industry. The institute now has a staff of 360 and an annual research budget of more than US\$50 million. There are nine departments in the institute, and the author visited the Advanced Technology Research Department where meetings were held with Dr Kiyoshi MINAMI, the General Manager of the department, Dr Kazuo OKAMURA, a Senior Research Engineer, Mr Masaharu TASAKI, a Research Engineer and Machiko MORISHITA, from the Public Relations Division. Dr Okamura has been developing

bioreactors that make use of sulphate-reducing bacteria [13]. These reactors may have significant potential for the treatment of high sulphate mine waste waters [14 - 17].

### **3.7 Tokyo - Chiba Institute of Technology**

This is a private university, and the author visited the Department of Civil Engineering, where a meeting was held with Dr Kazuo TAKI, an associate professor in this department. He is interested in removing metal ions from mine waste waters by using calcium hydroxyapatite as a cation-exchanger. The work is at a very preliminary stage, and so far no column experiments have been performed, nor any experiments to recover the metals and regenerate the calcium hydroxyapatite.

### **3.8 Tokyo - University of Tokyo**

This is a very big state university, regarded as the most prestigious in Japan. The author visited the Department of Chemical Engineering and met with Dr Shoji KIMURA, a professor in this department, and an expert in membrane technology. Dr Kimura has a great deal of experience in the use of membrane technology for desalination of seawater, and is interested in using this technology for the recovery of metals from mine waste waters, and for the clean-up of industrial effluents [18 - 22].

### **3.9 Tokyo - Sophia University**

This is a large private Catholic university. The author visited the Faculty of Science and Technology and met with Dr Yasuhiko KURUSU who is the professor of industrial organic chemistry. He is interested in the synthesis of new surfactant and flotation agents that may be of use in the treatment of mine waste-waters. Dr Kuruso had no specific proposal in mind, but expressed a general interest in collaboration.

### **3.10 Tokyo - Ochanomizu University**

This is a big private university and the author visited the chemistry department, where a meeting was held with Dr Isamu MATSUMOTO who is the professor of biochemistry. His interests lie more in the area of studying the toxic effects of mine wastes rather than their treatment and purification.

### **3.11 Tokyo - The Dowa Mining Company**

The Dowa mining company was founded in 1884 and is today one of the leading mining and smelting companies in Japan, which has diversified into the manufacture of high-tech materials such as superconductors, LEDs, magnetic materials and compound semi-conductors. The company also markets the technologies it has developed in the mining and smelting processes and in the treatment of waste materials from mining, milling and smelting. During the visit to Dowa Mining, meetings were held with Yoshiro WATANABE, a geologist who is a Senior Manager in the

Mineral and Energy Resources Department, Kazu IWANO, a metallurgist who is also a Senior Manager in the same department, Chihiro INOUE a microbiologist and metallurgist who is a manager in that department and Toshikazu SHIRATORI from the Environmental Technology Department.

Dowa Mining developed and patented [12] the process used at the Matsuo mine for bacterial oxidation of iron(II). The Canadian patent expires in 1997. A copy of this patent is included as an Appendix to this report.

### **3.12 Tokyo - Waseda University**

Waseda University is the most highly-rated of the private universities in Japan. An interview was arranged with Dr Akira HIRATA, who is a Professor of Chemical Engineering, and the Founder and Director of the Environmental Safety Centre. This centre has operated for about 14 years, and treats metal-containing wastes from the university's science and engineering departments. Six months ago, a new centre was set-up with funding from the NEC electronics company, who also have two staff-members on-site. Electronics companies wish to keep the content of their effluents confidential since this information can reveal closely-guarded industrial secrets. So NEC is interested in the development of a waste-treatment plant which can remove metals from waste waters. The new plant has replaced the older one, and has been designed to incorporate the lessons learned from the previous years of operating experience.

The wastes are batch-treated by either the ferrite or iron powder processes [23 - 26] after a preliminary analysis, carried out in the analytical chemistry laboratory which is part of the centre.

## **4 TREATMENT TECHNOLOGIES**

### **4.1 The Matsuo Mine**

#### **4.1.1 Background**

While a mine is in operation, pollution controls are usually in place and the environment is protected, but once production ceases, mines may be left without such controls. Waste water is left to flow from old mine stopes or tailings dams and pollution may continue long after the mine is closed. The old Matsuo Mine, which was once the largest sulphur mine in Asia, is an example of such an abandoned mine-site. A large outcrop of native sulphur was discovered in 1882 near Mt Iwate in Iwate Prefecture, some 450 km north of Tokyo. Mining of sulphur and iron sulphide (pyrite and marcasite) began shortly thereafter. By 1914, the Matsuo Mining Co., Ltd was established and full-fledged mining operations began. At first, only the sulphur ore was mined and processed, but in 1921, mining and processing of the sulphide ore commenced. Around 1955, when production peaked, about 1 million tons of crude ore was mined and 80,000 tons of refined sulphur were produced each year. At that time, about 4,000 workers were employed and the population around the mine-site reached about 15,000 (mine-workers and dependents). However, beginning in 1958, the demand for sulphur dropped. Then in 1965, cheap sulphur produced by the desulphurization of heavy oil came onto the market, gravely affecting the operations of Matsuo Mine. To reduce costs, the Matsuo Mining Co. switched from underground mining to open pit mining. In spite of this, production costs were still too high, and the company ceased operations in 1971 and closed down the mine. During the lifetime of the Matsuo Mine, some 29 million tons of ore and 2.5 million tons of refined sulphur were produced over a period of 60 years. Mineral deposits in this area are volcanic hydro-thermal metasomatic deposits and the ore reserves total over 200 million tons with an average grade of 40% sulphur. Some 27 million tons of ore have been excavated and thus the remaining ore reserves total more than 150 million tons. The deposits are embedded in lava and clastic rocks of two pyroxene andesite and are distributed in four zones. The upper part of the deposits is rich in sulphur while the lower part is mainly iron sulphide. The deposit has the form of an irregular circular disc with a diameter of about 1,500 m and a thickness of from 25 to 250 m, dipping towards the east.

#### **4.1.2 Mining Methods**

The room and pillar mining method was adopted for the primary stoping and the cut and fill method was adopted for the secondary.

For the primary stoping, drifts were excavated in grids of 100 m from east to west, and 33 m from north to south. In each ore block measuring 66 m from south to north and 100 m from east to west, 5 working areas were set up. Each working area had dimensions as follows: 10 m wide by 6 m high by 56 m in length. The ore production per working area was 8,400 tons representing a recovery of 22.6%. Horizontal roof pillars 6 m thick were left between levels.

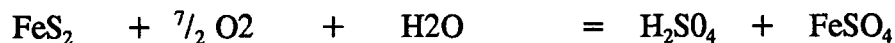
Overhead cut and fill and sublevel stoping were adopted as the secondary stoping methods to recover the horizontal pillars left by the primary stoping. This raised the recovery to 47%.

### 4.1.3 Environmental Effects

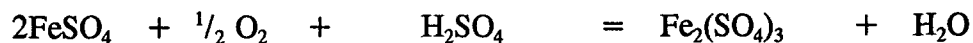
During the initial stages of the operation, the most serious threat to the environment came from the flue gases created from the sulphur-refining step. But with the full-scale development of the 112 meter level drift in 1916, the volume of waste water increased dramatically. By 1934, the pollution was noticeable at Morioka City, 40 kilometres downstream. In 1960, the flow rate of waste water from the mine was 30 m<sup>3</sup> per minute, with a pH of 1.6. The Matsuo Mining Company made some efforts to neutralize the wastes with slaked lime, and to divert some of the effluent underground. But these steps were insufficient, and indemnities had to be paid to local residents, farmers and fishermen to compensate for the damages caused to human health, agriculture and the fresh water fishery. Once the mine was closed, the rudimentary neutralisation procedures and indemnity payments stopped, and the pollution worsened. At the point where the Matsukawa river carrying mine effluent joined the Kitakami river, a rusty-brown stain of precipitating ferric hydroxide continued downstream for miles. The abandoned Matsuo mine site contained various sources from which contaminated water could flow :

- The mine workings, with a combined drift length of 345 km representing an excavated volume of some 13 million m<sup>3</sup> with a residual ore reserve of about 150 million tons.
- The open-pit site with an area of 236,000 m<sup>2</sup>
- Two waste rock dumps containing a total of about 6.9 million m<sup>3</sup> of low grade ore and overburden.
- A sludge dump containing 5.4 million m<sup>3</sup> of sludge from the pyrometallurgical processing of iron sulphide.

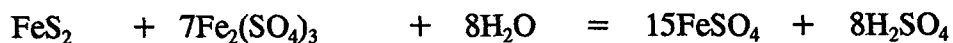
The various iron sulphides and sulphur species comprising the ore body are unstable once exposed to air and moisture. The complex chemical reactions taking place at the surfaces of the ore left in the mine and in the various dumps may be represented by the following series of equations. It should be noted that the Matsuo Mine contains a large amount of marcasite which is particularly susceptible to oxidation. The first step in the process is the oxidation of iron sulphide :



The next step is the oxidation of ferrous iron to ferric iron :

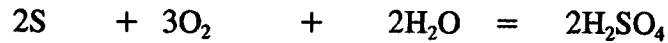


This step occurs very slowly at the low pH values found in acid mine waters, but may be catalyzed by the naturally-occurring chemoautotrophic iron bacterium *thiobacillus ferrooxidans*. The ferric iron produced can then cause the dissolution of more iron sulphide :



These last two reactions constitute a cycle for the dissolution of iron sulphide. Finally, the

elemental sulphur present in the mine and dumps may also oxidise in a bacterially-catalyzed process :



Thus, the overall result when mine walls, waste rock and sludge undergo wet oxidation by coming in contact with rain water, surface water and oxygen in the air is the production of an acidic solution of ferrous and ferric sulphate. The Matsuo Mine is located in an area of heavy snowfall and as the snow melts from April to June, the volume of mine water reaches its peak as does the total pollutant load on the environment.

#### **4.1.4 Treatment of Matsuo Mine drainage waters.**

In 1971, the Iwate Prefectural Government requested the Central Government to do something about mining-related pollution from the Matsuo Mine. The government considered this matter with the related agencies including the Forestry Agency, the Ministry of International Trade and Industry, the Ministry of Construction, the Ministry of Home Affairs and the Environmental Agency. As a result of these consultations, it was decided that government expenditure was essential and that a state-of-the-art treatment plant would be designed and constructed on the former Matsuo mine site. In the design of the treatment plant, it was decided to utilise the technology pioneered by the Dowa Mining Company at its Yanahara pyrite mine. At the same time, the importance of reducing the flow of rain and surface waters into the mine was recognised, and a comprehensive drainage scheme was laid out in order to reduce the quantity of contaminated water leaving the site.

##### **i) Drainage.**

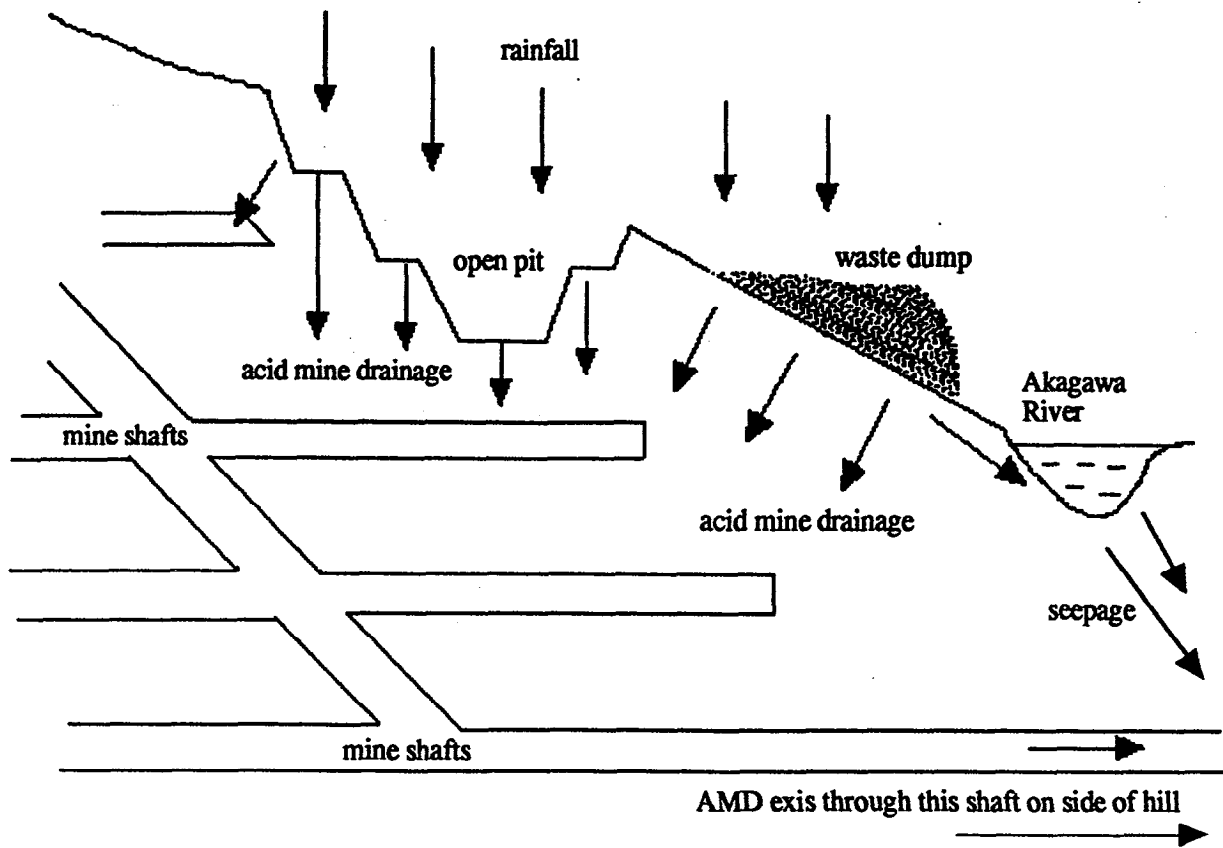
From the outset, it was realised that reducing the amount of river and surface water draining into the mine and dumps would give a corresponding reduction in the amount of water contaminated and requiring treatment. The strategy adopted to achieve this aim was as follows :

- plug and seal off the mine tunnels and stopes at the lower levels
- surface sealing, soil reclamation, and re-vegetation at the open pit site
- surface sealing, soil reclamation, and re-vegetation at the waste dump site
- construction of a three-sided concrete lining in the river, up-stream of the mine to prevent seepage of uncontaminated water into the mine.
- construction of a drainage channel across the side of the mountain up-stream of the mine to prevent seepage of uncontaminated water into the mine.

Figures 2 and 3 are schematic diagrams of the situation prevailing at the Matsuo mine site before and after drainage and reclamation work.

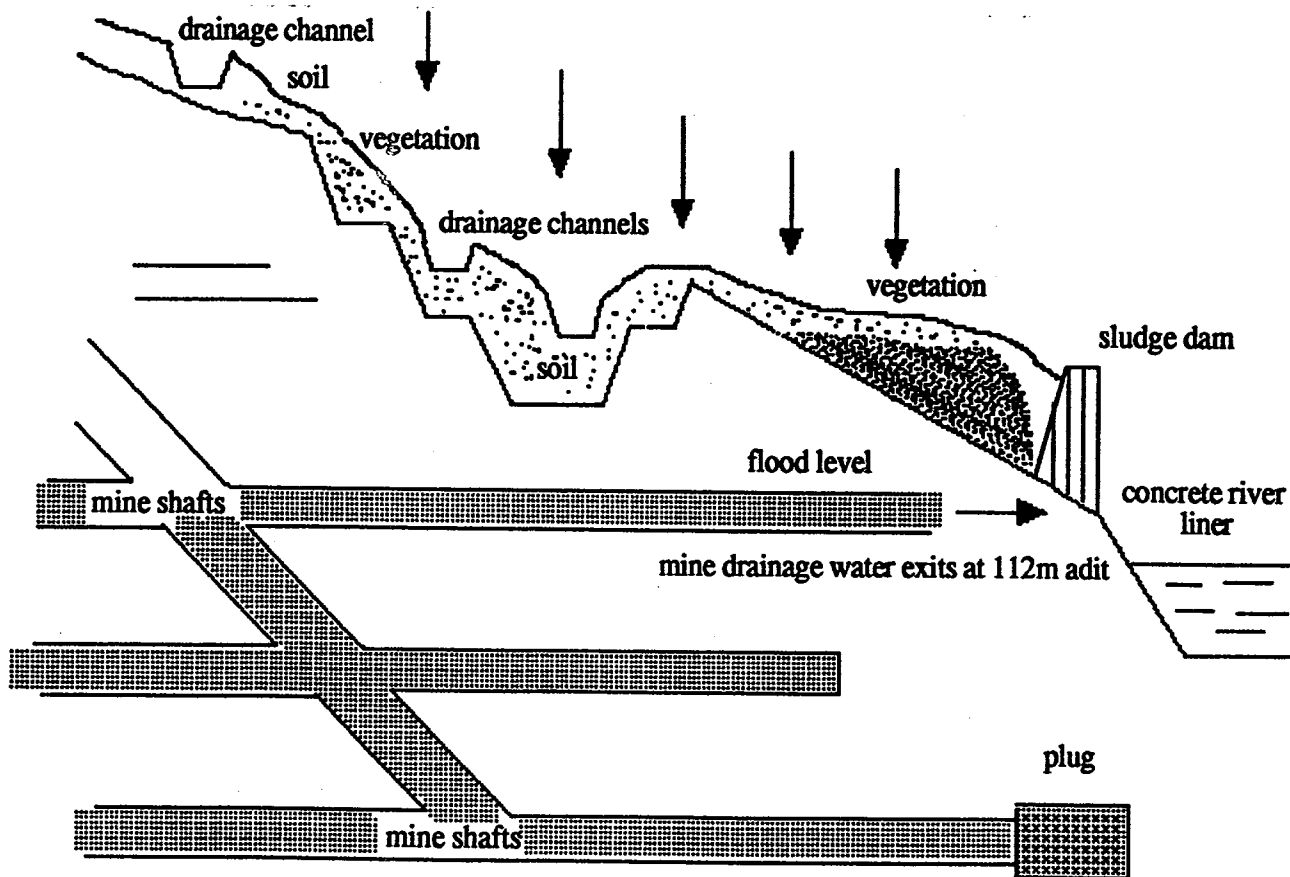


**Figure 2** The Matsuo mine site before drainage and reclamation



The first step taken was to install concrete plugs in the lowest horizontal shaft (the 3 m level). After this drainage adit was closed in 1970, the water level rose about 100 meters in 4 months so that nearly half of the 200 meter high cavity was filled with water and the waste water flowed out from the adit at the 112 m level instead. Since this had the effect of cutting off a large volume of the exposed ore to oxygen, and of reducing the underground catchment volume, the quality of the waste water improved, and the volume produced decreased steadily. The next problem to be tackled was that of the open pit site. This is a large horse-shoe shaped basin with a mining cavity just below it. The pit acted rather like a funnel, and collected rain and surface waters, directing them into the underground adits and cavities, where the action of the air and water on the exposed ore would frequently cause spontaneous combustion. To prevent this, the entire surface of the exposed orebody was reclaimed to a stable condition and then covered with soil and vegetation. In addition, drainage channels were set up inside the pit to collect and discharge rain

**Figure 3 The Matsuo mine site after drainage and reclamation**



overcome by lining the river bed and sides with concrete. Finally, a drainage channel was constructed around the mountain above the mine site, to intercept the run-off from higher up the mountain and direct it into the river below the mine. Water flowing from the 112 m level had by now caused some rock falls and cave-ins, and so a permanent drainage tunnel 322 m in length and lined with concrete was built. Inside this tunnel the waste water was contained in a 600 mm diameter pipe line made from rigid PVC. The construction of the drainage tunnel and pipeline took 18 months and cost some 600 million yen (at that time, about Can\$4 million). The work was completed in 1984.

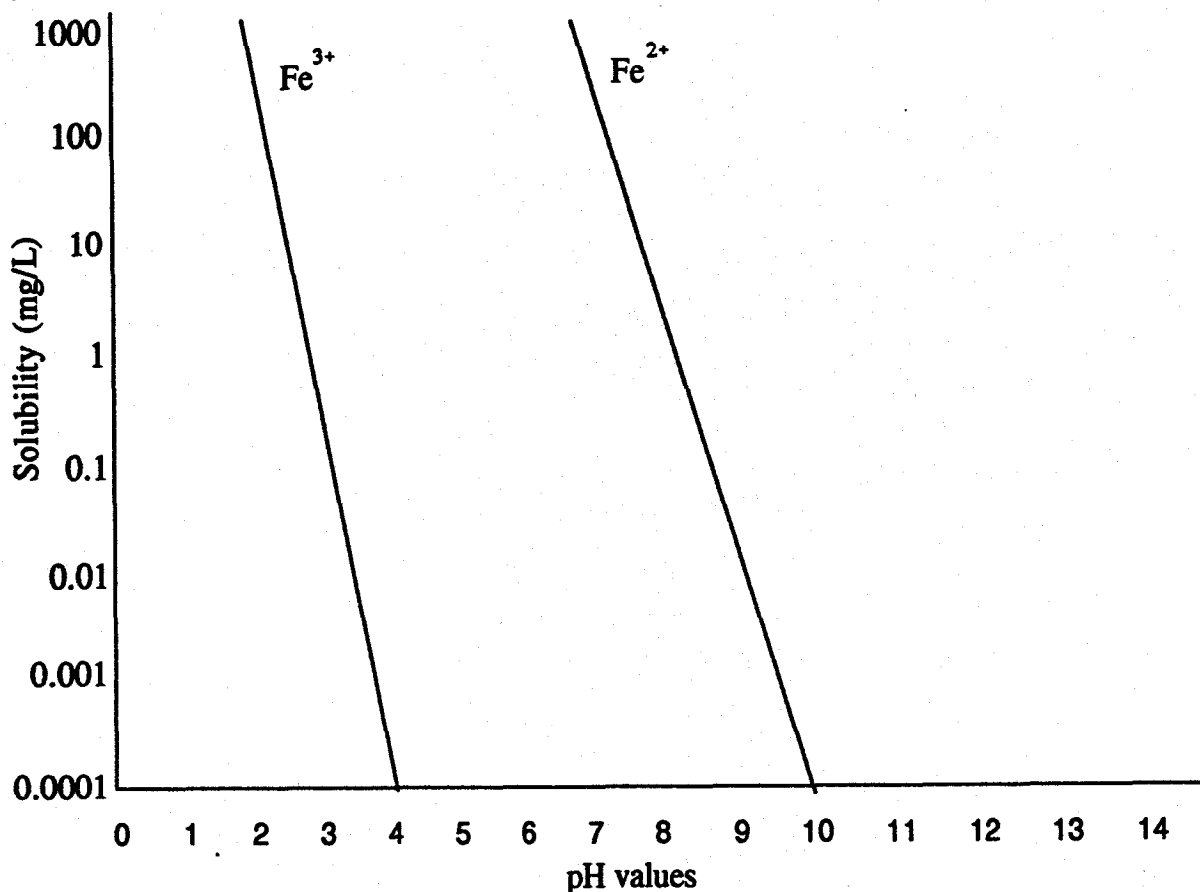
#### **4.1.5 The Treatment Plant**

The precipitation of iron as insoluble hydroxide is more readily achieved if the iron is present as Fe(III) rather than Fe(II). This is because Fe(III) hydroxide will precipitate out at a pH of around 4 whereas for the Fe(II) hydroxide to precipitate, the pH must be raised to 8 or above, as shown in Figure 4.

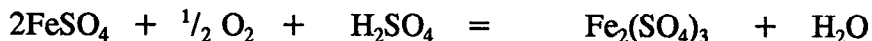
Calcium carbonate can be used as a neutralizing agent, and will raise the pH to about 5 - sufficient to cause the precipitation of Fe(III) hydroxide. But for Fe(II) hydroxide to be precipitated, other

agents are required, slaked lime ( $\text{Ca(OH)}_2$ ), for example. However, slaked lime is considerably more expensive than calcium carbonate, and the precipitates formed by slaked lime have poorer settling-out characteristics than those formed by calcium carbonate. Thus oxidation of  $\text{Fe(II)}$  to  $\text{Fe(III)}$  prior to hydroxide precipitation is desirable. In the original Yanahara mine treatment plant, nitrogen dioxide gas produced by the oxidation of ammonia was used to oxidise  $\text{Fe(II)}$  to  $\text{Fe(III)}$ . In 1974, the process was changed and a bacterial oxidation unit was installed. This made use of *thiobacillus ferrooxidans* to carry out the ferrous-ferric oxidation. This bacterial oxidation system uses basic ferric sulphate, generated by the hydrolysis of ferric sulphate in the oxidation tank, as a cell carrier for the microbes. It is precipitated and continuously recycled in the oxidation circuit. In this unit, the bacterial concentration in the oxidation circuit is maintained at about  $10^8$  cells per mL. (The natural concentration of these bacteria in the Akagawa river can be as high as 250,000 cells per mL). The unit is capable of oxidising more than 95% of the ferrous iron when treating mine water of pH 2.5 containing 2100 mg/L of ferrous iron with a flow rate of  $1.2 \text{ m}^3$  per minute. The operating cost of the bacterial oxidation plant was about 30% that of the nitrogen dioxide unit. An improved version of this bacterial oxidation unit was designed for the new treatment plant at the Matsuo mine. The construction work on this plant was started in 1977 by the Iwate Prefectural Government and subsidized by the Ministry of International Trade and Industry. It was completed in 1981 at a total cost of about 9.3 billion yen (about Can\$40 million at that time). The plant has four identical systems, each capable of handling a flow rate of  $7 \text{ m}^3$  /min of waste water, giving a total handling capacity of  $28 \text{ m}^3$  /min. The first step in the

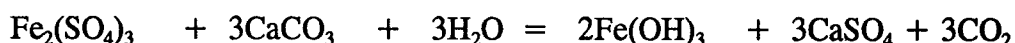
Figure 4 The variation in solubility of iron hydroxides with pH



treatment is the distribution tank where the flow is split equally among the four systems. The oxidation tanks follow, where the water comes into contact with high concentrations of *thiobacillus ferrooxidans* which has been cultivated on the surface of iron sludge from the neutralization tanks. The water/sludge mix is agitated and aerated by jets of air. The ferrous iron is oxidised during this stage :



The mix then passes to the settling tanks, from which the supernatant goes on to the neutralization tanks, and the bacteria-laden sludge is recycled to the oxidation tanks. In the neutralisation tanks, a suspension of calcium carbonate (ground to <325 mesh) is run in through a thin pipe with an adjustable valve, at a rate calculated to deliver exactly the quantity necessary to raise the pH to 4. The neutralization reaction is as follows :



The large quantities of iron sludge formed during the neutralization step are settled out in the solid-liquid separation tanks which come next in the treatment scheme. Coagulants are added as required, to speed-up the settling process. The separation tanks are circular and made of concrete. From here, the solids are pumped up to the sludge storage dam. The dam was built by dredging and excavating a swamp adjacent to the plant. This is an inclined core type rock-fill dam with the natural topography as the east-west embankment and utilizing earth and rocks from the site as the south-north embankment. The dam is was designed to hold all the sludge generated over a twenty-year period, and has a capacity of about 2 million m<sup>3</sup>. The pH of the overflow water from the separation tanks is once more adjusted to 4 (the natural pH of the Akagawa river downstream from the plant), and is now ready for discharge into the Akagawa river. The target of this new neutralization plant was to improve the waste water quality to meet environmental standards, which demand a pH value between 6.5 and 8.5, and an arsenic content of less than 0.05 ppm in the Kitakami River, downstream of the Akagawa River. These targets are met. The facility operates 24 hours a day, all year round. There are some 32 workers and managers working three 8 hour shifts. There is a central control room, and many of the operations may be remote-controlled from this location. Some 9,000,000 m<sup>3</sup> of waste water are treated each year, at a cost (1992) of about 600 million yen. This works out to be about 95 cents (Canadian) per m<sup>3</sup> of water treated.

## 4.2 Ferrite and Hematite Production at Matsuo

### 4.2.1 Introduction

The large quantities of ferric hydroxide sludge produced by the treatment plant at the Matsuo mine will eventually fill the sludge storage dam. In order to delay this eventuality, and also in the expectation of generating some income from the treatment plant, MMAJ sponsored a research project to produce marketable ferrite/magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite from the ferric hydroxide sludge. Because of its unusual magnetic properties, ferrite can be used as a paint to lay tracks that

can be used as a guidance system for driverless trolleys, or for the blind. Hematite,  $\text{Fe}_2\text{O}_3$ , is used as a pigment, and for polishing surfaces as jewellers' rouge.

#### 4.2.2 Ferrite Production

Ferrite production may be considered in six stages, as shown in Figure 5 :

i) pre-treatment of the waste-water to remove Al and As. This is carried out by pH control. The pH is adjusted to 6, and the solution is aerated. The Al and As compounds both precipitate out under these conditions, as shown in Table 1 :

**Table 1      Pretreatment**

	Fe (ppm)	Al (ppm)	As (ppm)
Before treatment (pH 2.1)	390	80	1.9
After treatment (pH 6)	290	< 1	0.002

ii) formation of Fe(II) hydroxide - some of the mine waste-water is made basic to pH 10, to cause the precipitation of ferrous hydroxide. This is allowed to settle out and later mixed with ferric hydroxide (see iv) to produce ferrite.

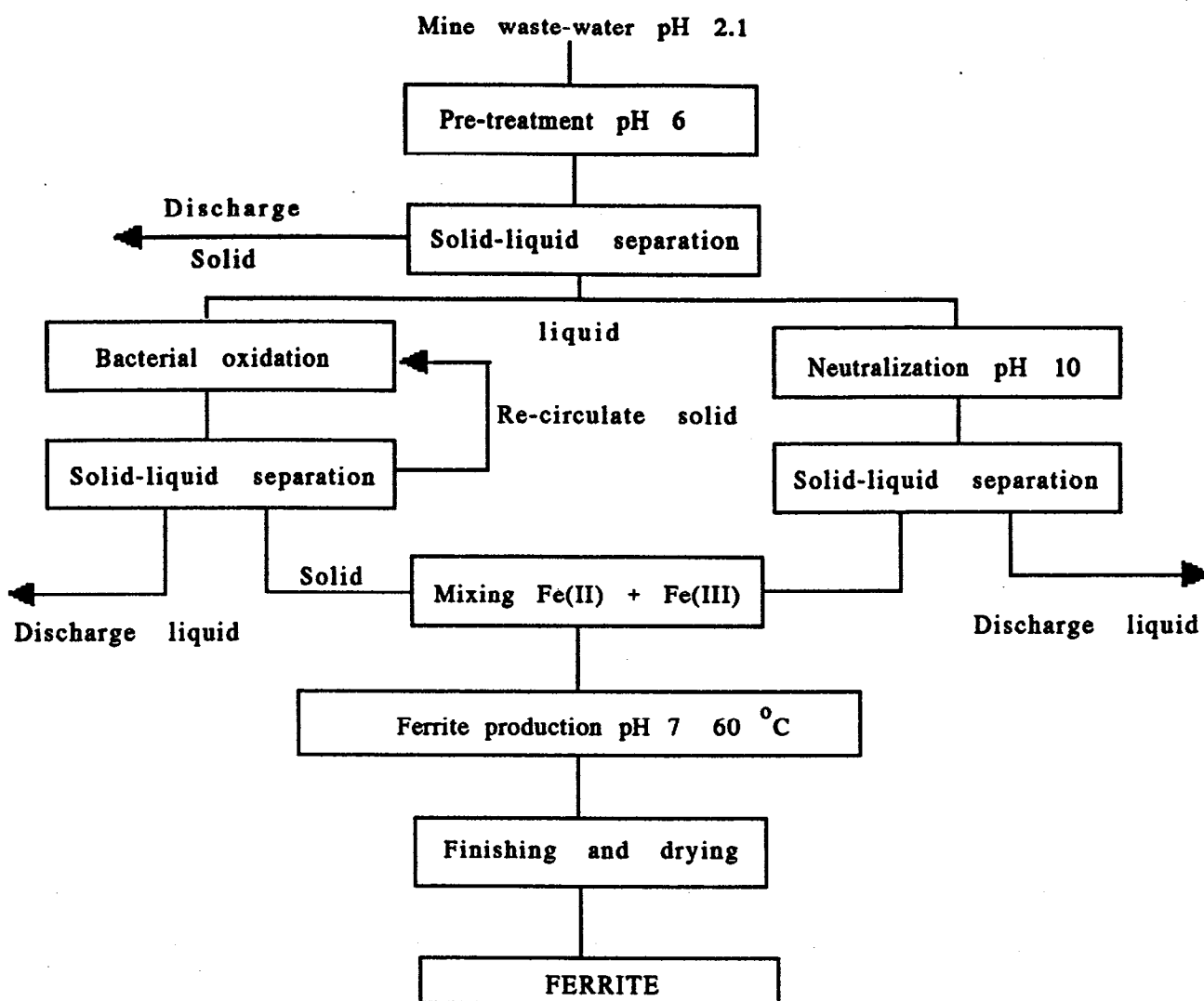
iii) formation of ferric hydroxide - the Fe(II) in the mine water undergoes oxidation by *thiobacillus ferrooxidans*, calcium carbonate is added and ferric hydroxide is produced as previously described.

iv) the ferric and ferrous hydroxides are then mixed together in the ratio  $\text{Fe(III)/Fe(II)} = 1.5$ , the pH is adjusted to 7, and the mixture heated and stirred at  $70^\circ\text{C}$  for six hours whereupon a ferrite slurry forms.

v) separation of ferrite slurry - the ferrite slurry is separated from the other products (notably  $\text{CaSO}_4$ , gypsum) by magnetic separators.

vi) finishing - the ferrite slurry is stirred and aerated. It is then dehydrated to ferrite cake containing 80% moisture in a continuous belt process before being air-dried. The finished product has a magnetisation value of over 60 emu/g and a specific surface area of about  $30 \text{ m}^2/\text{g}$ . The recovery rate is about 440 g of ferrite material per  $\text{m}^3$  of waste-water.

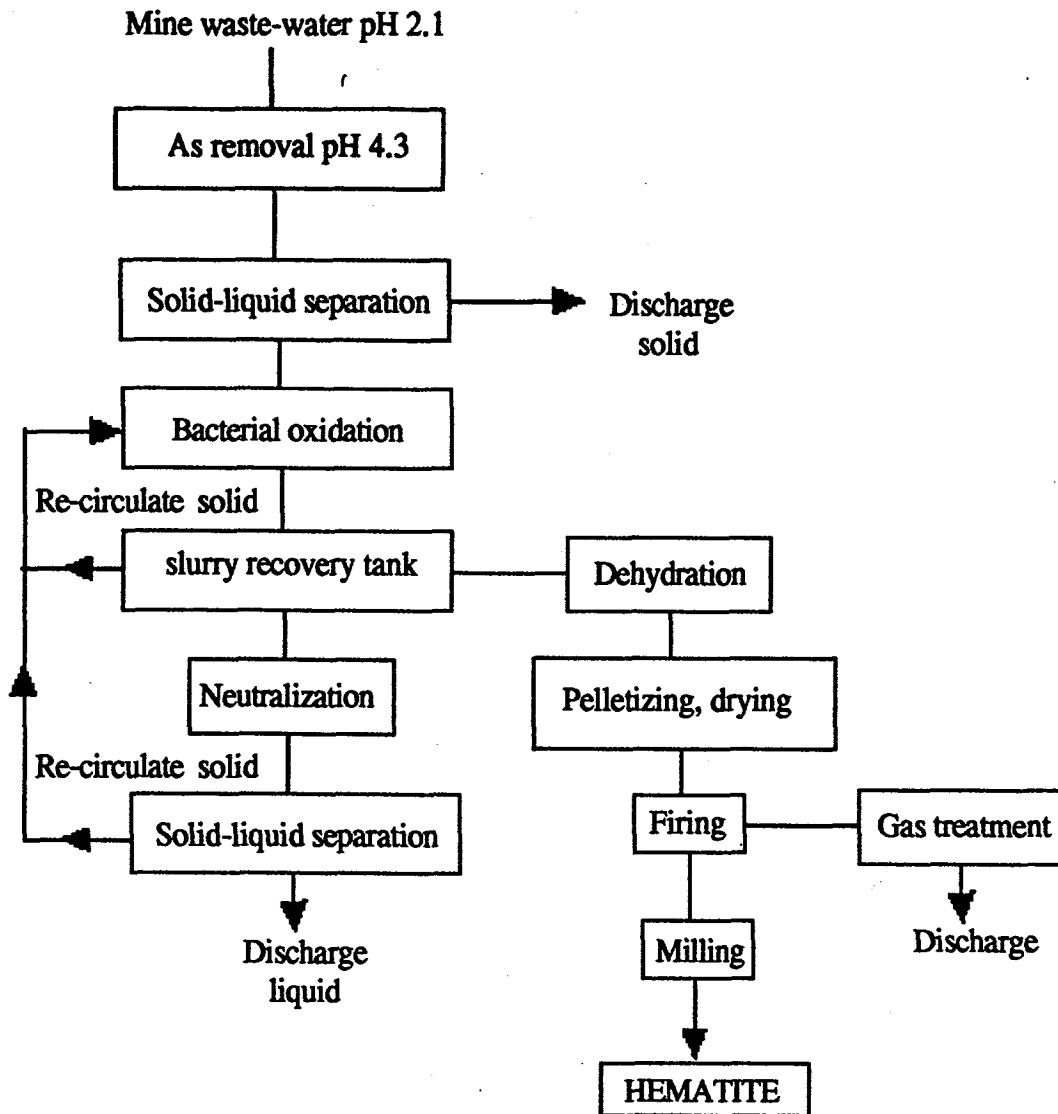
Figure 5 Ferrite production



#### 4.2.3 Hematite Production

An outline of the process is illustrated in Figure 6. The first stage is a pre-treatment step to remove arsenic. The pH of the mine drainage water is adjusted to about 4.3, and the water is aerated. The As is co-precipitated with some of the iron, and allowed to settle out. The next stage is bacterial oxidation and formation of ferric hydroxide - the Fe(II) in the mine water undergoes oxidation by *thiobacillus ferrooxidans*, as previously described. This is followed by the neutralization step, and then the separation of the ferric hydroxide in a settling tank. The ferric hydroxide is re-cycled through the oxidizing stage again, where it settles out in the slurry recovery tank and is the separated and sent to the de-watering/pelletizing/firing/milling circuit. Here it is dehydrated by suction in a belt system, pelletized and fired for 5 hours at 825°C prior to milling.

**Figure 6**      **The production of hematite**



The product is high quality and of acceptable colour for marketing. The production yield of hematite is about 370 g/m<sup>3</sup> of mine drainage water. This represents an annual projected output of some 3,000 tons of hematite from the Matsuo mine drainage water.

[NOTE : The ferrite and hematite production processes were fully researched and developed ready for production, but the cost of production was comparable to, or higher than prevailing market prices, so production was never started. But there is a market for ferric sulphate, which is used as a flocculant. The Dowa Mining Company markets an acidic ferric sulphate solution from its Yanahara operation, and recoups some 10% of treatment costs in this way.]

## 4.3 Sludge Densification

### 4.3.1 Introduction

Sludges are generally allowed to settle, and then separated from the waste water prior to some form of filtration or de-watering in order to reduce the volume and improve the mechanical properties of the sludge before dumping. The settling-out and filtration rates of sludges are dependent on particle size and shape characteristics. Larger, more spherical and less porous particles settle and filter faster, and give rise to a denser sludge with a low moisture content. Typically, in the treatment of acid mine drainage, a sludge is produced during the neutralization step. Following neutralization, there is a settling tank. It has been found that if sludge from the settling tank is re-circulated to the neutralization tank, then the quality of the resulting sludge is improved.

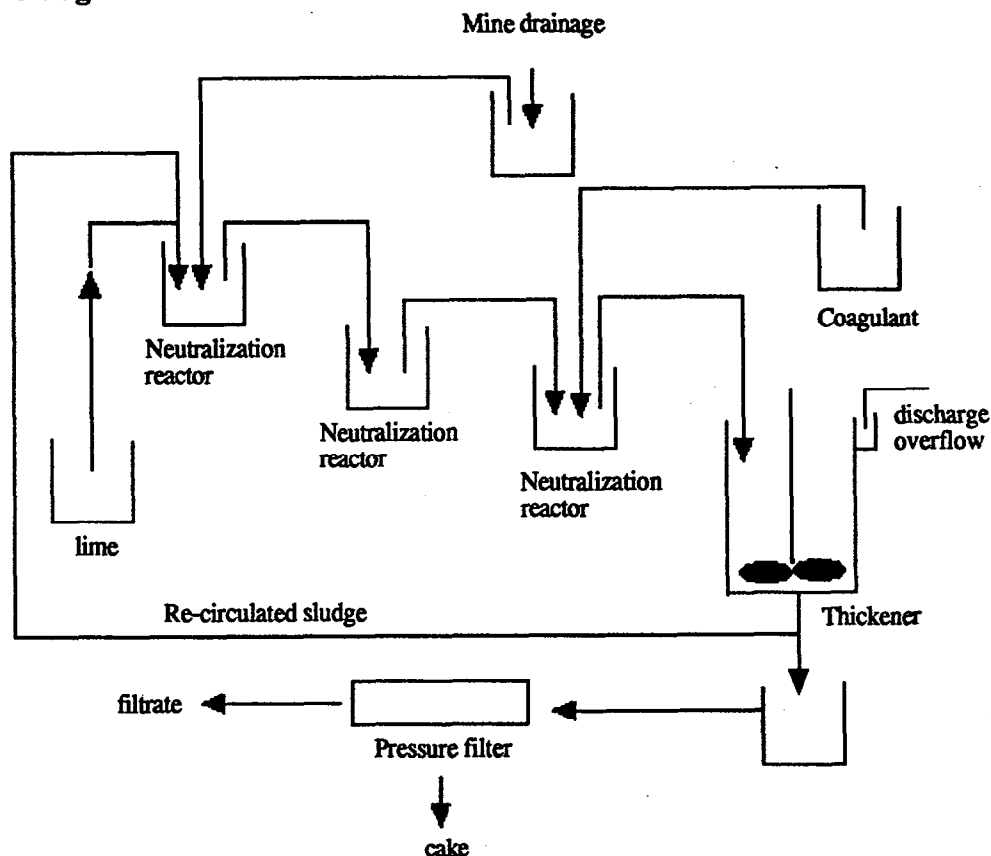
### 4.3.2 Method and Test Results

MMAJ has sponsored a series of tests of this effect. A schematic of the test circuit used is shown in Figure 7.

During the tests, the amount of sludge re-circulated varied from 0 - 60% in increments of 20%. The results showed some interesting trends :

- When the sludge was being re-circulated, for each level, the quality of the sludge extracted improved with time, over a period of days.

Figure 7 Sludge densification circuit





- The improvement was more marked as the proportion of sludge re-circulated increased.
- Sludge densification was more readily achieved in heavily polluted water.
- The denser sludges filtered more quickly and produced solids with a higher specific gravity and lower moisture content.

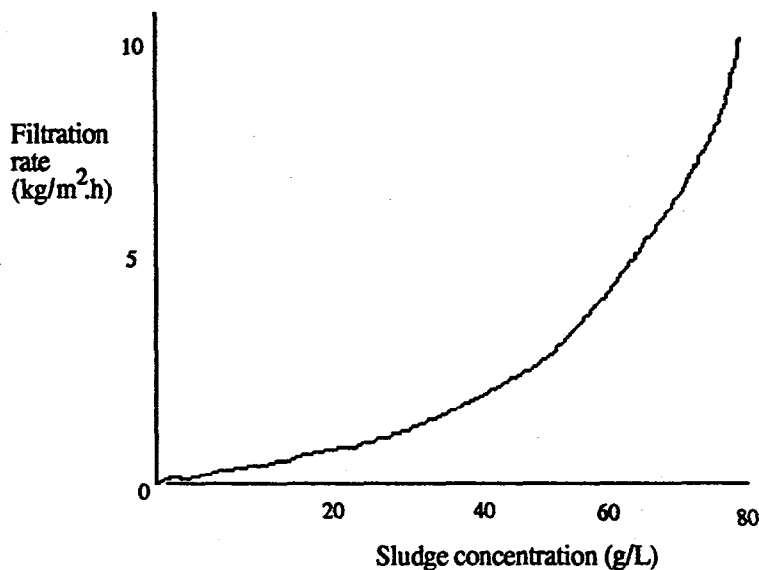
Some sample test results are given in Table 2

**Table 2 Sludge densification test results**

Test Period (day)	Sludge Conc (g/L)	Pulp Sp. Gravity	Solid Sp. Gravity
2 - 10	13.1	1.0071	2.18
11 - 20	25.8	1.0172	3.00
21 - 30	42.1	1.0286	3.12
31 - 40	56.6	1.0393	3.27
41 - 50	70.4	1.0503	3.50
51 - 55	74.4	1.0529	3.46

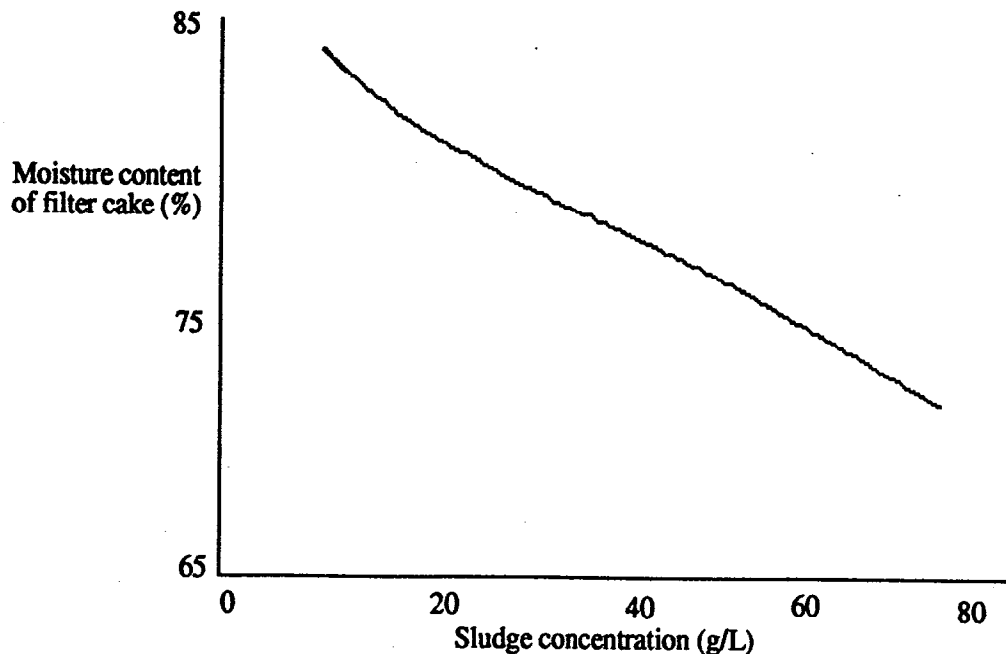
The observed variation in filtration rate with sludge concentration is shown in Figure 8.

**Figure 8 Variation of filtration rate with sludge concentration**



The decreasing moisture content of the filtered cake with increasing sludge concentration is shown in Figure 9

**Figure 9 Dependence of cake moisture content on sludge concentration**



#### **4.4 The Ferrite and Iron Powder Methods of Mine-Waste Treatment**

##### **4.4.1 The Ferrite Process for Waste Water Treatment**

Ferrite has a *spinel* structure. The spinels form a large class of compounds whose structure is related to that of the mineral spinel itself,  $MgAl_2O_4$ . The general formula is  $AB_2X_4$  and the unit cell contains 32 oxygen atoms in an almost perfect cubic close packed (ccp) array, ie  $A_8B_{16}O_{32}$ . In the normal spinel structure, 8 metal atoms (A) occupy tetrahedral sites and 16 metal atoms (B) occupy octahedral sites and the structure can be regarded as being made up of alternating cubelets of ZnS-type and NaCl-type structures. The two factors that determine which combinations of atoms can form a spinel-type structure are a) the total formal cation charge and b) the relative sizes of the two cations with respect both to each other and to the anion. For oxides of formula  $AB_2O_4$  charge balance can be achieved by three combinations of cation oxidation state :  $A(II)B(III)_2O_4$ ,  $M(IV)M(II)_2O_4$  and  $M(VI)M(I)_2O_4$ . The first combination is the most commonly-encountered, and examples are known with :

A(II) = Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Sn  
B(III) = Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni, Rh.

Many spinel-type compounds do not have the normal structure in which A are in tetrahedral(t) sites and B are in octahedral(o) sites; instead they adopt the inverse spinel structure in which half the B cations occupy the tetrahedral sites whilst the other half of the B cations and all the A

cations occupy the octahedral sites, the author.e.  $[B]t[AB]_6O_4$ . The occupancy of the octahedral sites may be random or ordered. Several factors influence whether a given spinel will adopt the normal or inverse structure, including a) the relative sizes of A and B b) the Madelung constants for the normal and inverse structures c) ligand field stabilization energies of cations in tetrahedral or octahedral sites and d) polarization or covalency effects. An enormous range of compounds with normal or inverse spinel structures are known, and that replacement of one cation by another is possible, without any appreciable distortion or reduction in stability of the lattice as a whole. Thus if spinel-type compounds are formed *in situ* in the presence of cationic impurities in solution, the spinel or inverse spinel lattice in course of formation constitutes an ideal host for the entrapment or encapsulation of these unwanted metal ions within a stable crystal lattice, allowing for their removal from solution. This is the basis for the Ferrite Process of waste-water treatment. The inverse spinels of formula  $AFe_2O_4$  are known as ferrites. An important example is the black compound  $Fe_3O_4$  (the mineral magnetite) in which the Fe(II) ions all occupy octahedral holes, and the Fe(III) ions are evenly divided between the octahedral and tetrahedral sites. During the ferrite waste-water treatment process [23 - 26], ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) is added to the mine waste water in sufficient quantity to give an excess concentration of Fe(II) over the combined impurity metal ions of about from ten to twenty times. The pH of the solution is adjusted to between 9 -11, it is heated to about 65°C, stirred and air is blown through the solution. Under these conditions, part of the Fe(II) is oxidised to Fe(III), and when the stoichiometric proportions are right, a precipitate of ferrite will be produced. This will consist of a lattice of  $Fe_3O_4$ , with impurity metal ions incorporated into the lattice. The ferrite sludge will coagulate and settle. Magnetite,  $Fe_3O_4$ , is strongly ferromagnetic, and this property is shared by the ferrite sludge which may therefore be separated magnetically from the treated water. Environmental regulations are strict in Japan, and many universities and technical institutes treat laboratory effluents prior to releasing them to the environment through the drainage system. The treatment plant at Waseda University is run by. Dr Akira HIRATA, who is a Professor of Chemical Engineering, and the Founder and Director of the Environmental Safety Centre. This centre has operated for about 14 years, and treats metal-containing wastes from the university's science and engineering departments. Six months ago, a new centre was set-up with funding from the NEC electronics company, who also have two staff-members on-site. Electronics companies wish to keep the content of their effluents confidential since this information can sometimes reveal closely-guarded industrial secrets. So NEC is interested in the development of a waste treatment plant which can remove metals from waste waters. The new plant has replaced the older one, and has been designed to incorporate the lessons learned from the previous years of operating experience. Each laboratory collects its wastes in 20 L plastic vessels, labels them with an estimate of what they contain, and delivers the vessels to the centre. Once there, they are analyzed in the centre's laboratory by atomic absorption spectroscopy, and the vessels are grouped into batches containing similar metal contaminants. These are then batch-treated by either the ferrite or iron powder (see later) processes. Sometimes the two methods are used sequentially on the same batch. The ferrite process can treat waste waters with total concentrations of above 2,000 ppm of mixtures such as Cu, Zn, Pb, Cd, Ni, V, Cr, Mn. [Some metals or metalloids such as Hg and As do not respond well to this treatment and remain in solution. Wastes containing these elements are treated by the iron powder method.] The ferrite method can reduce the metal ion content of such a mixture from 2,000 ppm down to less than 5 ppm in a single treatment. The ferrite sludges produced must be disposed of in dump-sites,

but the metals held in the lattice do not readily leach out.

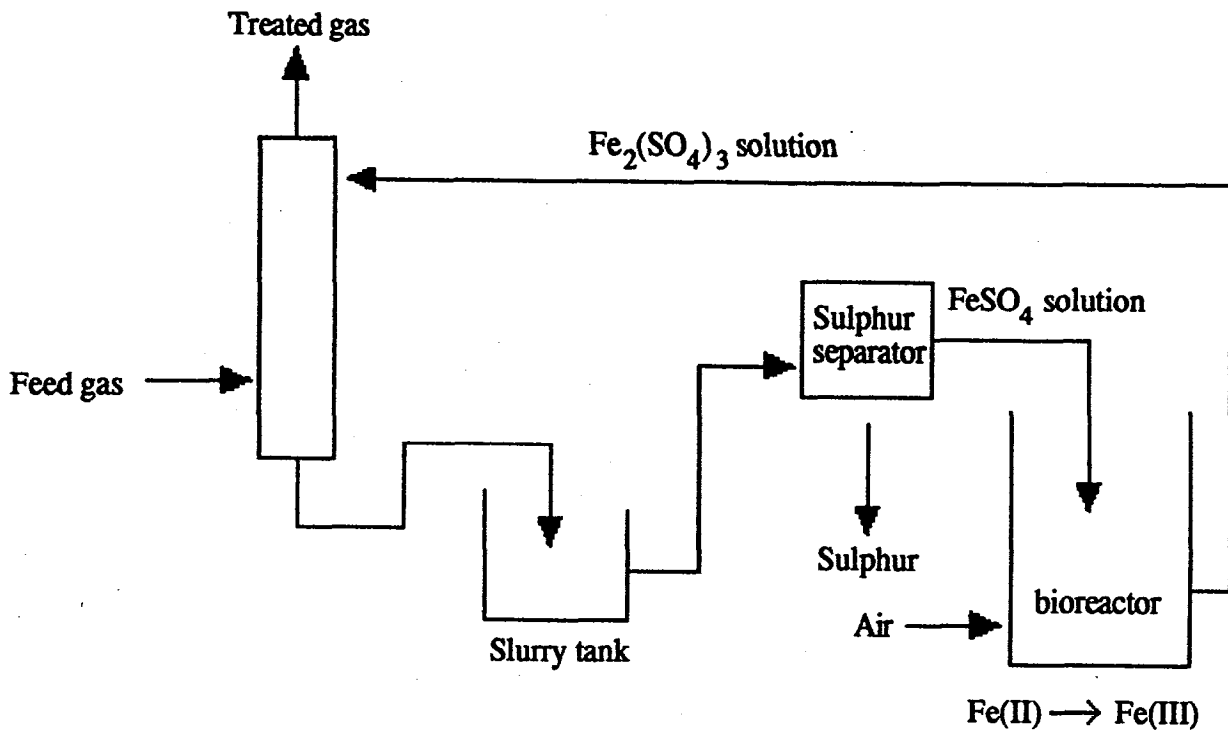
#### 4.4.2 The Iron Powder Process

This process is used in the Waseda University plant, often in tandem with the ferrite process, to deal with solutions containing very high levels of metal contaminants, and for solutions containing precious metals, As and Hg - the method may be used for solutions containing more than total concentrations in excess of 10,000 ppm. After analysis to determine metal content, a calculated stoichiometric excess of iron powder is added to the solution, whereupon the iron reduces those less electropositive metal cations to the elemental form. Then the solution is made basic, and the iron precipitates as a hydroxide, forming a sludge which contains the contaminating metals as co-precipitates. This insoluble residue is then filtered off under pressure, giving treated water which may subsequently be treated by the ferrite process, if necessary.

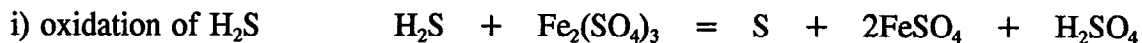
#### 4.5 Treatment of Flue-Gases using Ferric Sulphate

The Dowa Mining Company has developed [27] a de-sulphurization treatment for flue gases containing  $H_2S$ . Essentially, the treatment consists of spraying the flue gases with ferric sulphate solution, which oxidises the sulphide to elemental sulphur, and leaves ferrous sulphate. This is then run through a bioreactor containing *thiobacillus ferrooxidans*, and re-oxidised to the ferric state, ready for re-circulation to oxidise more flue gases. The process thus continually re-cycles the iron sulphate solution. A schematic flow-sheet is shown below in Figure 10

Figure 10 Flue gas de-sulphurization



The overall chemical reactions involved are as follows :



ii) regeneration of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>



The process has been patented in both the US [29] and Japan and has been licensed by Dowa exclusively to the NKK Corporation of Tokyo [27].

#### 4.6 The Application of Iron-oxidizing Bacteria to Hydrometallurgical Flue Dust Treatment

The flash furnace at the Dowa Mining Company's Kosaka smelter treats 13,600 T/M (tons/month) of domestic and imported copper concentrate containing Au, Ag, Cu, Pb, Zn, Fe, As, Sb, Cd and Bi. To prevent the accumulation of impurities, 1,470 T/M of flue dust containing Cu, Pb, Zn, Fe, As etc (this figure includes some 370 T/M from other companies), along with 1,400 T/M of lead concentrate, 740 T/M of residues from other processes and 4,200 m<sup>3</sup>/M of waste water (from the sulphuric acid plant) is treated using hydrometallurgical processes. At one stage in the process, arsenic and iron are precipitated. The leached solution is neutralized to pH = 5 with calcium carbonate and steam-heated to 50 °C while jets of air are blown into the solution. However, there are some problems with this method;

(i) much energy is consumed to keep the solution at 50 °C (ii) the cost of taking the pH to 5 is high, because much calcium carbonate remains unreacted (iii) more than 30% of the zinc present in the solution co-precipitates with the iron at this pH and (iv) a large volume of sludge is formed. Previously, bacterial oxidation of the iron prior to precipitation had not been considered as feasible, since the solution conditions would inhibit bacterial growth - the average concentrations of F<sup>-</sup> and Cl<sup>-</sup> ions in the solution exceed the tolerance limit of normal *Thiobacillus ferrooxidans* strains. In order for the bacterial oxidation method to be applicable, new strains of *Thiobacillus ferrooxidans* needed to be developed, with improved tolerances to these ions. This was achieved, and strains which could multiply in the presence of 200 ppm of F<sup>-</sup> (normal tolerance level 20 ppm) and 5,000 ppm of Cl<sup>-</sup> (normal tolerance level 1,000 ppm) were grown by a process of gradual acclimatization. To recycle the iron oxidizing bacteria, diatomaceous earth is used as a carrier of cells. The cells are concentrated together with the diatomaceous earth in the settling process, and recycled to the oxidation circuit. Since the bacterial iron oxidation process was introduced, a new arsenic removal method has been developed - this involves addition of ferric iron to the solution in a pre-treatment step, which enables arsenic to be precipitated by pH control prior to the bacterial oxidation ( since As inhibits this process). The new process was proved with a 1/1000 scale pilot plant which operated for a year, and is now in operation, giving improved cost-effectiveness and zinc recovery.

## **4.7 Ion-Exchange Technology**

Toshishige Suzuki [1, 2] of the Government Industrial Research Institute, Tohoku (GIRIT), has carried out some fairly extensive research into the use of selective ion-exchange resins for the separation of rare-earth metals. These metals must often be extracted from low-grade ores, and so resins with a high concentration efficiency coupled with high selectivity are required. Resins with such properties could also be used in waste-water treatment, as well as more generally in the developing field of hydrometallurgy. In comparison with solvent-extraction systems, the ion-exchange resins have some inherent advantages, notably their greater concentration efficiencies, and the ease of phase separation. But at present, the range of resins available with good selectivity for particular metals is limited. Hence the need for new resins to be developed. In a recent article [1] the GIRIT group describe their work with previously developed resins of three types :

- i) chelating polymer resins
- ii) chelating-reagent loaded ion-exchangers
- iii) reagent-incorporated resins

This work is continuing at GIRIT and other Japanese research institutes and is considered to be a very promising field which is expected to become the method of choice for rare-earth metals extraction, and then later to become increasingly important for hydrometallurgy and the extraction of metals from mine and industrial waste waters.

## **4.8 Membrane Technology**

### **4.8.1 Introduction**

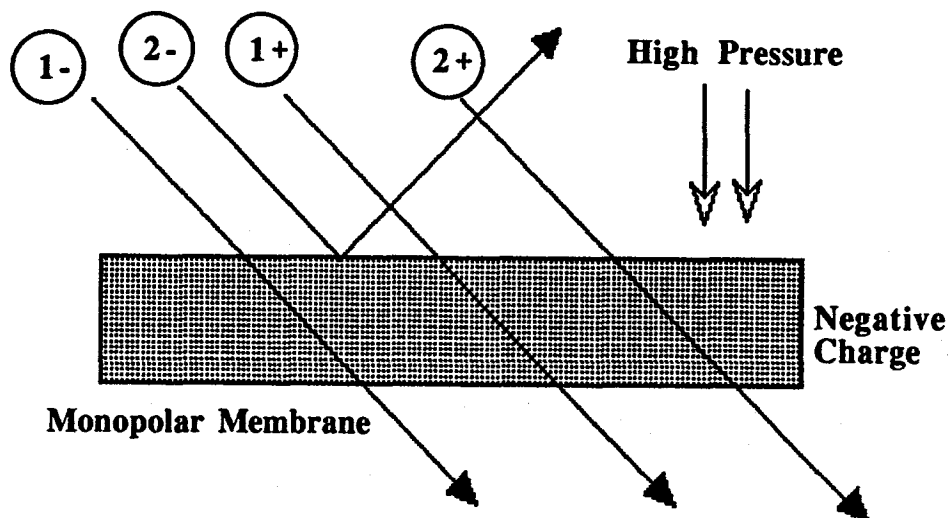
Membrane technology has developed enormously over the past twenty years, and is widely used in desalination for the production of drinking water from seawater, and in the production of "distilled" water for industrial uses. New membranes now being developed may well prove useful in removing metal ions from industrial and other wastes, allowing the recovery of useful quantities of metals [18 - 22]. Membranes are very sensitive to the presence of solid particles, which can cause pore blockage, so membrane methods will certainly involve a pre-treatment stage. There is also a problem with highly-charged ions being attracted to sites in the membrane, and reducing separation efficiency. But in spite of these inherent difficulties, research in to the development of new membrane techniques continues, and shows great promise for the future.

### **4.8.2 Bipolar reverse osmosis membranes for separating mono and divalent ions**

Charged reverse osmosis membranes have many fixed charged groups in them, therefore they can separate solutes of almost the same size or molecular weight according to their electrical polarity (positive charge, negative charge or neutral ). However, neutral membranes cannot separate such

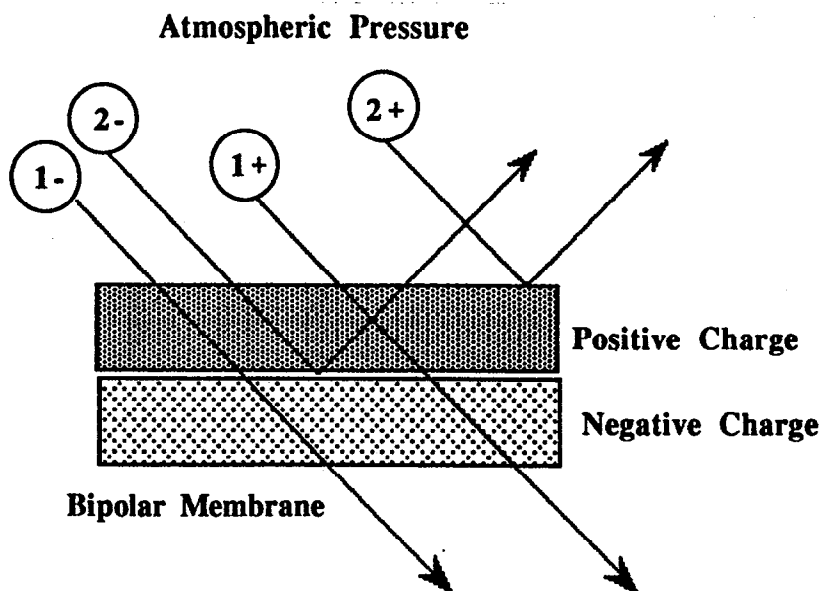
solutes because their separation mechanism is due to a "sieve effect". But the selectivity towards mono- and divalent ions of charged reverse osmosis membranes is provided by the electrical interaction between the membranes and the electrolyte. Previous experiments and theoretical calculations using both single and mixed electrolytes have demonstrated that negatively charged membranes show satisfactory selectivity towards monovalent and divalent anions, but that cation selectivity is poor. More recent experiments with bipolar membranes have shown that these are capable of more efficient separations of cations [22]. A repulsive force on anions and an attractive force on cations occur for the ions carried with the permeate volume flow. In particular, divalent anions receive a stronger repulsive force than other ions and are prevented from entering the membrane. Therefore, in the case of negatively charged membranes, the rejection of the divalent anion is high, but that of the divalent cation is poor. In the case of a positively charged membrane, the opposite effects are observed. A model for a negatively charged monopolar membrane is shown in Figure 11.

**Figure 11** Rejection Model for a Monopolar Membrane



A rejection model for a bipolar membrane is shown in Fig.12.

**Figure 12 Rejection Model for a Bipolar Membrane**



Cations receive Donnan repulsion from the positively charged layer and are rejected. Anions are rejected by the negatively charged layer. Consequently, as divalent ions receive stronger Donnan repulsion than monovalent ones, selectivity towards mono- and divalent ions is achieved. Bipolar reverse osmosis membranes that have both negatively and positively charged layers have been prepared to enhance the selectivity towards mono- and divalent ions in respect of both cations and anions. Positively charged layers are formed on low pressure reverse osmosis membranes having negative charge (NTR-7410 and 7450) by an adsorption method using polyethyleneimine (PEI) or a quaternary ammonium polyelectrolyte (QAP). These layers attach to the membrane's dense layer, which is made of sulphonated polyether sulphone. The selectivity of mono- and divalent ions is proven by experimental results for some single electrolytes ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{MgCl}_2$ ). Although negatively charged membranes repulse divalent anions more strongly than cations and monovalent anions, bipolar reverse osmosis membranes reject both divalent cations and divalent anions better than monovalent ions. An optimal preparation method for bipolar membranes showing selectivity towards mono- and divalent ions was developed. The bipolar membranes showed good ion selectivity for artificial sea water.

## **4.9 Bacterial Oxidation or Reduction Techniques**

### **4.9.1 Iron Oxidising Bacteria**

The group of researchers at Iwate University in Morioka led by Dr Tatsuo Omura are carrying out extensive studies for the improvement of the ferrous iron bacterial oxidation process in use at the nearby Matsuo Mine treatment plant [8]. Their studies focus on the development of a fluidised bed reactor for immobilising the *Thiobacillus ferrooxidans*. Their experiments have included comparisons of a variety of support media for the fluidised bed in the reactor, followed by temperature and pH studies. They conclude that the synthetic resin Amberlite IRA-398 is the best



support medium. Their results show that using a fluidised bed reactor, retention times for complete oxidation can be reduced to about 20 minutes. The tests were carried out at the bench scale, but pilot-plant studies are planned for next year.

#### 4.9.2 Sulphate-Reducing Bacteria

The metal salts present in mine drainage waters in many locations are present as sulphates. If the sulphate present in the water is reduced to sulphide, much of the metal present in solution will precipitate out as insoluble sulphide, since many common metal sulphides are insoluble. Thus, both the sulphate and metal ions could be removed in what amounts to a single step. Certain anaerobic bacteria have the power to reduce sulphate to sulphide. There is currently a great deal of interest in the pursuit of this technology in Japan, notably by MMAJ, the Dowa Mining Company and the Shimizu Corporation [13]. Some pilot-scale experiments have already been carried out, with very encouraging results. Waste water from the Yanahara mine was treated in a continuous-flow system with a fluidized bed anaerobic bioreactor with a working volume of 180 L. After treatment, Fe(II) and Zn(II) levels had dropped from about 50 ppm down to less than 0.2 ppm, and it appeared that the precipitation of metal ions as sulphides did in fact occur, as predicted. During these experiments, the sulphate-reducing bacterium strain used was *Desulfovibrio vulgaris*, and the nutrient was a mixture of sodium lactate and yeast extract. Current research efforts are proceeding along the following lines :

- identification and cultivation of new strains of suitable bacteria that can operate at lower temperatures. Because of its volcanic nature, with a high natural occurrence of sulphur compounds, Japan is a good source of these naturally-occurring bacteria.
- finding cheaper nutrient mixtures that will cut the cost of the process
- process modifications to reduce the Chemical Oxygen Demand (COD) of the treated effluent. In most reported results, this has so far been unacceptably high.
- the development of more efficient bioreactors

[NOTE : these bacteria are also of interest because their ability to reduce sulphate with the production of sulphide can have a negative influence on the performance of methane-producing bacteria.]

#### 4.9.3 Sulphur-Oxidising Bacteria

The bacterium *Thiobacillus thiooxidans* can oxidise sulphide to elemental sulphur. A futuristic design project envisaged by planners at the MMAJ proposes a combination bioreactor for the complete treatment of mine drainage problems in a very ingenious fashion. In the first (upper) level of the reactor, algae use photosynthesis for the generation of carbohydrates which subsequently provide fuel for two heterotrophic bacterial systems. The first of these makes use of the sulphate-reducing bacterium *desulfovibrio*, which produces hydrogen sulphide causing the precipitation of the heavy metals in the drainage water as insoluble sulphides. Excess hydrogen sulphide then rises, where it is oxidised to sulphur by *thiobacillus thiooxidans*. The sulphur precipitates out and is recovered. Thus the one bioreactor removes both metals and sulphate from the drainage water.

This is a design project only at this stage, but feasibility studies are proceeding.

#### 4.10 Metal-Absorbing Organisms

Certain molds have the capability of absorbing metals. Extensive research has been carried out in Japan in this area by MMAJ, culminating in a pilot-plant project involving a continuous treatment for manganese by rotating discs covered with mold. The results were excellent for reducing manganese levels, but the nutrient costs were high and the mold used showed little tolerance for the presence of other heavy metals, making real-world applications difficult. More resistant mold strains and cheaper nutrients are being sought.

#### 4.11 Deep-Mine Injection

The idea was to pump mine wastes into deep shafts with no treatment whatsoever. It was considered that for very deep areas underground, the wastes would then be effectively removed from contact with the biosphere. Shortly after the project commenced, government regulation banned the practice. One important part of the project was to develop a computer model of the way underground waters were transported naturally. Once the major part of the project stopped, the funding was diverted to this part of the project, which has continued and reached a successful conclusion with the development of a software package which can simulate underground water movement under varying sets of geological parameters.

#### 4.12 Mine-Stopes for Waste Storage

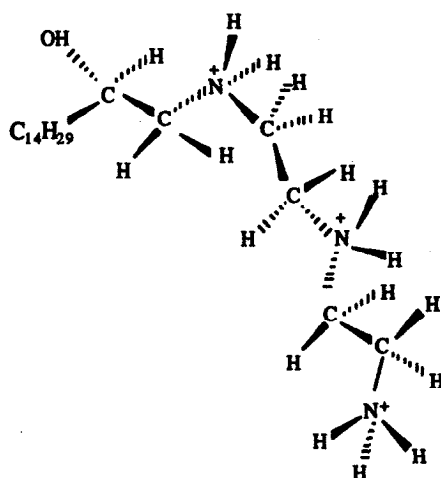
The need to identify disposal sites for mine sludges and solid industrial wastes is pressing in Japan. Abandoned mine sites are obvious candidates. But each mine site is different, with different geological characteristics and potential. Disposal sites are designed specially for each location, and careful studies of the possibilities of percolation of leachates and contamination of ground waters are carried out during the preliminary site-identification procedures. Government regulations are strict, but some abandoned mines will almost certainly be used for this purpose.

#### 4.13 Flotation technology.

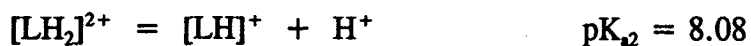
Katsuyoshi Mori of the Government Industrial Research Institute, Tohoku (GIRIT) has developed a flotation system for the removal of metal ions from acid mine waters [3 - 7, 28]. After extensive testing of a range of reagents, the surfactant/sequestering agent used in this system is N-(b-hydroxyhexadecyl) diethylene triamine:

$C_{14}H_{29}C(H)(OH)CH_2NH(CH_2)_2NH(CH_2)_2NH_2$ . Under acidic conditions, this would protonate and exist in the triply-charged cationic form shown below in Figure 14:

**Figure 14 The protonated flotation agent**

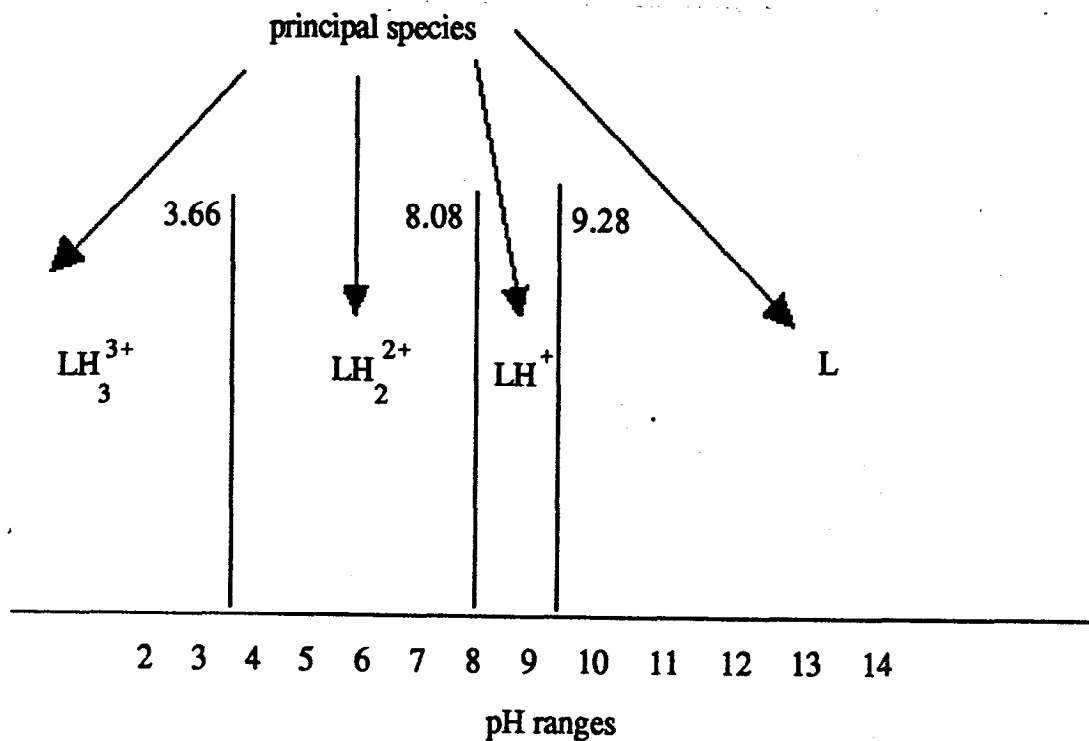


According to Mori's work, the acid dissociation constants are :



Thus a principal species diagram for the system would be as shown in Figure 15 :

**Figure 15 A principal species diagram for the flotation agent**

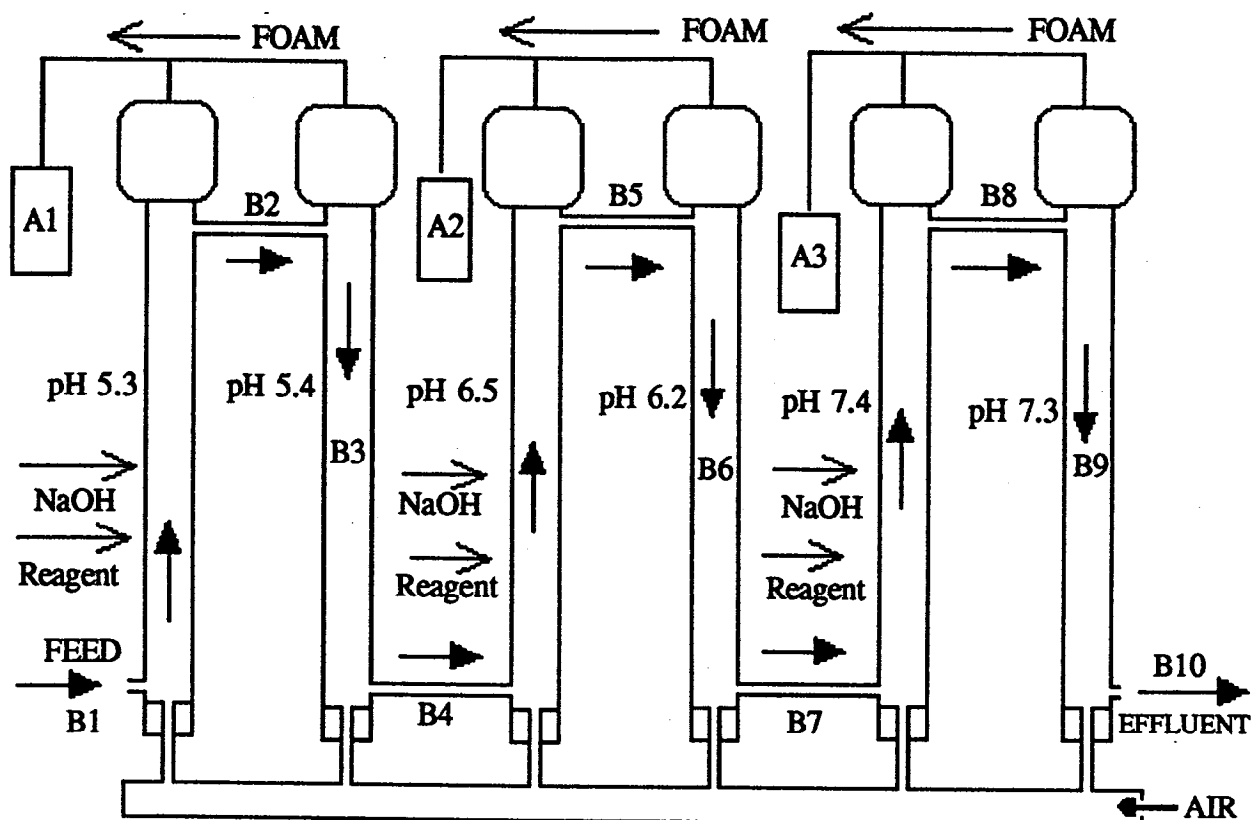


Mori has calculated formation constants for complexes with 1:1 and 2:1 ligand : metal ratios with this reagent for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  at pH 12 and the values found are :

	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$
$\log K_{ML}$	14.1	8.1	8.1
$\log K_{ML_2}$	9.8	7.8	8.2

Mori and his associates have carried out quite extensive studies on this system, including measurements of the Langmuir adsorption parameters for the ligand and the metal chelates, optimisation of bubble flow rate, pH studies and design of flotation vessels. The final tests were performed on the mine drainage water at the Kosaka complex of the Dowa Mining Company for a month-long period. The prototype system consisted of six linked flotation columns 5 cm in diameter and 180 cm high. The operating conditions were as follows : reagent, N-(b-hydroxyhexadecyl) diethylene triamine; addition rate of reagent, equivalent to 7 mg/L of Cu; flow rate of mine water, 200 mL/min; flow rate of air, 2 L/min (in each column); pH values in the 1-2, 3-4 and 5-6 column pairs were set at 5, 6 and 7 respectively by NaOH addition. A schematic diagram of the apparatus is shown below in Figure 16.

Figure 16. Linked flotation columns for mine water tests



Waste-water feed is pumped through from the lower left hand side in the Figure, and circulates through the six columns as shown by the arrows. Air is forced into the bottom of each column through a fritted disc, and the bubbles rise to the top, where the resulting foam is captured and drained off. Alternate columns have addition points for reagent and NaOH. The pH levels are monitored in each column. Copper, zinc, cadmium and iron levels were monitored throughout the month-long test, at the points illustrated in the Figure.

A summary of the results is given below, in Table 3.

**Table 3 Flotation test results**  
(metal ion concentrations are given in ppm)

Monitoring Point (Fig 13)	Cu	Zn	Cd	Fe
A1	126	3.5	0.5	24.4
A2	12.6	19.1	2.1	4.6
A3	5.6	55.4	84.0	10.0
B1	1.1	2.5	0.4	13.5
B2	0.4	1.9	0.4	14.7
B3	0.14	2.3	0.3	12.5
B4	0.16	2.3	0.3	14.6
B5	0.08	1.7	0.3	10.5
B6	0.02	1.7	0.3	9.8
B7	0.06	1.9	0.23	10.8
B8	0.03	0.4	0.07	3.9
B9	0.01	0.5	0.05	2.6
B10	0.01	0.5	0.00	1.9

A summary of the results is shown below in Table 4.

In addition , measurements of sulphate concentration were performed on the feed and on the final effluent. These were 236 ppm and 137 ppm, respectively.

These results demonstrate that the method is capable of reducing metal concentrations to acceptable limits, and at the same time, producing fairly Table 4

**Summary of results from Table 3**

metals	Cu	Zn	Cd	Fe
Feed (ppm)	1.1	2.5	0.4	13.5
Effluent (ppm)	0.01	0.5	0.00	1.9
Foam (A1)	126	3.5	0.5	24.4
Foam (A2)	12.6	19.1	2.1	4.6
Foam (A3)	5.6	55.4	84.0	10.0

concentrated solutions from which metal recovery could be attempted. A larger scale column was also successfully developed and controlled. This allowed waste-water flow rates of up to 30 L/min, and air flow rates up to 180 L/min. This project ended in 1982, and no further funding was allocated to it. New government legislation is now leading to some reconsideration of flotation technology.

## **5 CONCLUSIONS**

- There is a high degree of environmental consciousness in Japan, and some treatment technologies applicable in Canada have been developed and are in place at mine and smelter sites.
- There are many research groups actively engaged in the development of new technologies for the treatment of mine drainage water. Many of these initiatives are of direct relevance to the Canadian situation. Much of the work is published internally, in Japanese.
- There is a great deal of collaboration and interaction between university, government and private sector research groups.
- Quite often, several groups in different institutions will be working independently on the same problem.
- There is a great deal of expertise for bringing ideas to the implementation/pilot plant stage and then on to commercial exploitation.
- Most research groups are well-funded and have impressive back-up infrastructure such as modern instrumentation and workshop facilities.
- All the groups contacted during this investigation expressed what appeared to be a genuine willingness for international collaboration in this field with Canadian researchers. Some funding for such collaboration is already available from both Japanese and Canadian government sources.
- Personal contacts are of paramount importance when dealing with the Japanese.

## **6 RECOMMENDATIONS**

- Collaboration between Japanese and Canadian researchers in this field should be encouraged and increased. Some mechanisms for collaboration are already in place and accepted, notably the Japan Science and Technology Fund (financed by Canada) and the International Joint Research Fund (financed by Japan). MEND researchers should be encouraged to apply for funding from these sources. In addition, some MEND funds should be set aside for joint Canadian-Japanese collaboration specifically in the field of acid mine drainage research. This would best be done in concert with MMAJ, who may agree to match MEND funding.
- Contact should be established between MEND and MMAJ administrators with the objective of setting up a new funding source for Japan-Canada Collaborative Acid Mine Drainage Research. This should be by face-to-face meetings in the first instance, so that personal relationships can be established. Once this has been achieved, then guidelines with respect to the mechanisms of the new joint research scheme (ie funding, selection, ownership of technologies developed, patents etc.) should be agreed upon.



## 7 REFERENCES

- 1) T. Suzuki and H. Matsunaga, *Trends in Inorganic Chemistry*, **33**, 2 (1991)
- 2) Y. Wakui, H. Matsunaga and T. Suzuki  
in "Solvent Extraction - ISEC'90" (Ed. T. Sekine) Elsevier 1992 pp 937-942.
- 3) K. Mori, S. Sasaki and T. Tadaki  
*J. Soc. Mat. Eng. Res. Japan*, **3**, 58 (1990)
- 4) K. Mori, *GIRIT Reports (Tohoku)*, **3**, 15 (1986)
- 5) K. Mori, *Akita Kagaku Gijutsu Kyo Kaishi*, **38**, 2 (1986)
- 6) S. Sasaki and K. Mori, *Akita Kagaku Gijutsu Kyo Kaishi*, **34**, 3 (1982)
- 7) K. Mori, S. Sasaki and H. Yamazaki,  
*J. Mining and Metallurg. Inst. Japan*, **103**, 87<13> (1987)
- 8) T. Omura, T. Umita, V. Nevov, J. Aizawa and M. Onuma,  
*Wat. Sci. Tech.*, **23**, 1447 (1991)
- 9) K. Nakamura, T. Noike and J. Matsumoto, *Wat. Res.*, **20**, 73 (1986)
- 10) D.G. MacDonald and R.H. Clark, *Can. J. Chem. Eng.*, **48**, 669 (1970)
- 11) T. Imaizumi in "Bioengineering and Biotechnology Symposium No 16 (1986)"  
John Wiley & Sons 1986 (NY) pp363-371.
- 12) Canadian Patent 1076721.
- 13) M. Tasaki, Y. Kamagata, K. Nakamura, K. Okamura and K. Minami,  
*FEMS Microbiol. Lett.*, **106**, 259 (1993)
- 14) G.F. Parkin, M.A. Sneve and H. Loos, *Wat. Sci. Tech.*, **23**, 1283 (1991)
- 15) J.P. Maree and W.F. Strydom, *Wat. Res.*, **19**, 1101 (1985)
- 16) J.P. Maree and W.F. Strydom, *Wat. Res.*, **21**, 141 (1987)
- 17) G. B\_chard, S. Rajan and W.D. Gould, *Biohydrometallurgy* - In Press
- 18) T. Tsuru, S. Nakao and S. Kimura, *J. Chem. Eng. Japan*, **24**, 511 (1991)

- 19) T. Tsuru, M. Urairi, S. Nakao and S. Kimura,  
*J. Chem. Eng. Japan*, **24**, 518 (1991)
- 20) T. Yamaguchi, S. Nakao and S. Kimura, *Macromolecules*, **24**, 5522 (1991)
- 21) T. Tsuru, M. Urairi, S. Nakao and S. Kimura, *Desalination*, **81**,219 (1991)
- 22) M. Urairi, T. Tsuru, S. Nakao and S. Kimura,  
*J. Membrane Science*, **70**, 153 (1992)
- 23) K. Ito, T. Kanzaki, Y. Tamuara and T. Katsura,  
*J. Chem. Soc. Dalton Trans.*, 2217 (1981)
- 24) Y. Tamuara and T. Katsura, *Yousuito-Haisui*, **28**, 147 (1986)
- 25) Y. Tamaura, *Bull. Chem. Soc. Japan*, **59**, 1829 (1986)
- 26) Y. Tamuara, M. Kitamura and H. Takatsuki,  
*Industrial Water*, **367(4)**, 29 (1989)
- 27) *The Bio - SR Process*, NKK Corporation, Tokyo
- 28) W. Walkowiak in "*Innovations in Flotation Technology*"  
NATO ASI Series, Vol. E **208** (1992) pp 455-474
- 29) US Patent 4931262.

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- The author wishes to express his gratitude for the cooperation and hospitality extended by all the University, Government and Corporate groups with whom he met.
- Finally, the invaluable contribution of Hiroshi Suzuki in sharing his expertise and making all the arrangements for interviews and meetings in Japan are gratefully acknowledged.

*\* MEND (Mine Environment Neutral Drainage) is a tripartite programme which is jointly funded by the Canadian Mining Industry, the Federal Government of Canada and five of the Provincial Governments of Canada.*

**9 APPENDIX**

**Canadian Patent #1076721**



**Canadian Patent**

**Brevet canadien**

1076721

**To all to whom these presents shall come:**

Whereas a petition has been presented to the Commissioner of Patents praying for the grant of a patent for a new and useful invention, the title and description of which are contained in the specification of which a copy is hereunto attached and made an essential part hereof, and the requirements of the Patent Act having been complied with,

Now therefore the present patent grants to the applicant whose title thereto appears from the records of the Patent Office and is indicated in the said copy of the specification attached hereto, and to the legal representatives of said applicant for a period of seventeen years from the date of these presents the exclusive right, privilege and liberty of making, constructing, using and vending to others in Canada the invention, subject to adjudication in respect thereof before any court of competent jurisdiction.

Provided that the grant hereby made is subject to the conditions contained in the Act aforesaid.

In testimony whereof, these letters patent bear the signature of the Commissioner and the seal of the Patent Office hereunto affixed at Hull, Canada.

**A tous ceux qui les présentes verront:**

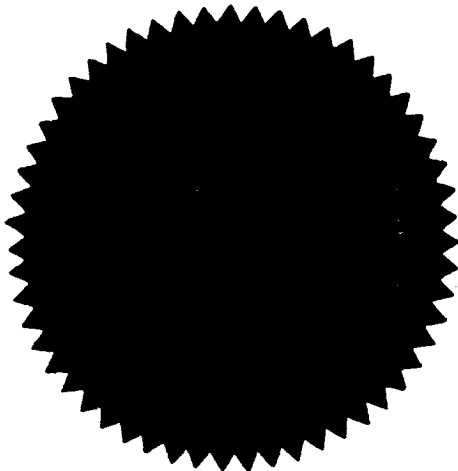
Considérant qu'une requête a été présentée au Commissaire des brevets, demandant la délivrance d'un brevet pour une invention nouvelle et utile, dont le titre et la description apparaissent dans le mémoire descriptif dont copie est annexée aux présentes et en fait partie essentielle, et que ladite requête satisfait aux exigences de la Loi sur les brevets,

A ces causes, le présent brevet confère au demandeur dont le titre de propriété audit brevet est établi d'après les dossiers du Bureau des brevets et est indiqué dans ladite copie du mémoire descriptif ci-annexé, et aux représentants légaux du dit demandeur, pour une période de dix-sept ans, à compter de la date des présentes, le droit, la faculté et le privilège exclusif de fabriquer, construire, exploiter et vendre à d'autres au Canada l'invention, sauf jugement en l'espèce par un tribunal de juridiction compétente.

La concession faite par les présentes étant soumise aux conditions contenues dans la loi précitée.

En foi de quoi ces lettres patentes portent la signature du Commissaire ainsi que le sceau du Bureau des brevets apposé à Hull, Canada.

APR 29 1980  
AVR



Commissioner of Patents    Commissaire des brevets

Attesting Officer    Certificateur

⑪ (A) No. 1076721

④⑤ ISSUED 800429

⑤② CLASS 362-13  
C.R. CL.

⑤① INT. CL. <sup>2</sup> C02C 5/10

①⑨ (CA) **CANADIAN PATENT** ①②

⑤④ PROCESS FOR OXIDATION TREATMENT OF Fe<sup>2+</sup> IN  
WASTE WATER

⑦⑩ Yabuuchi, Eizo; Fukuda, Katsutake,  
Japan

Granted to Dowa Mining Co., Ltd.,  
Japan

②① APPLICATION No. 239,957

②② FILED 751117

③⑩ PRIORITY DATE Japan (52308/1975) 750430

No. OF CLAIMS 3

1076721

This invention relates to a process for the oxidation with iron bacteria of the  $Fe^{2+}$  contained in mine and other similar factory effluents. In particular, the present invention is concerned with an improved process  
5 for waste water treatment wherein the iron bacteria grow on porous materials utilizing the  $Fe^{2+}$  in the waste water as the energy source, and the porous materials are repeatedly used to give efficient oxidation of the  $Fe^{2+}$  in the presence of the constantly highly dense bacteria  
10 population.

In general, it is extremely advantageous to oxidize  $Fe^{2+}$  to  $Fe^{3+}$  beforehand in treatment for pollution control of acidic waste waters which are discharged from metal mines, dressing and refining plants and the like. This  
15 is because much  $Fe^{2+}$  in the waste waters requires much neutralizing agent and makes the operation complicated.

Some ways of utilizing iron bacteria in the oxidation of  $Fe^{2+}$  in these acidic waste waters have been suggested. For example, a process wherein iron bacteria are  
20 liquid-cultured in a treated waste water and the culture is poured into other waste water is described in Japanese Patent Publication No. 44717/72. This process, however, has drawbacks in that the number of bacteria per unit amount of the waste water to be treated is reduced because  
25 the original bacteria solution is diluted upon being added to the waste water to be treated, and the cells are lost when the treated waste water flows out of the system since the process is based on liquid-culture; this results in a lower oxidation rate.

30 Japanese Patent Publication No. 38981/72 based on



the invention accomplished by the same inventors as of the present invention teaches a process to effect the oxidation of  $\text{Fe}^{2+}$  and the culture of bacteria at the same time by using in situ produced iron oxides as adsorbents of the bacteria and partially recirculating the adsorbents. This process is surely beneficial in a relatively high pH range, but does not work well in a waste water the pH of which is in a lower range (for example,  $\text{pH} < 2.0$ ) to insure low production of basic salts because the iron oxides are not present to work as adsorbents due to dissolution into the waste water to be treated.

In the drawings:

Figures 1 - 3 are rough views of the present systems in cross section; and Figure 4 is a graph showing the effect of the present process.

The reference numbers in Figures 1 - 3 have the following meaning.

- 1 ..... Oxidation tank (Oxidation and culture zone)
- 2 ..... Sedimentation tank (Sedimentation zone)
- 3 ..... Treated suspension delivering pipe
- 4 ..... Acid-resistant porous material return pipe
- 5 ..... Waste water inlet pipe
- 7 ..... Air pipe
- 14 ..... Oxidized waste water outlet pipe

The present invention provides a process without the above-mentioned drawbacks of the prior art. In this process, the oxidation rate (amount) is improved by continually maintaining a high bacteria content and this makes it possible to conduct simultaneously the oxidation of the  $\text{Fe}^{2+}$  in the waste water to be treated and the culture of



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the bacteria capable of oxidizing the  $Fe^{2+}$  effectively even in a lower pH and temperature range. Namely, the present invention is a process for the oxidation with iron bacteria of the  $Fe^{2+}$  contained in mine and other similar factory effluents at a pH so low as to provide little precipitation of basic salts, characterized by the following steps:

5 passing the stream of waste water to be treated to an oxidation and culture zone which includes beds of acid-resistant, porous and particulate material for the iron bacteria;

10 oxidizing the  $Fe^{2+}$  in said oxidation and culture zone by agitating and blowing air into the waste water with particles suspended therein to culture the iron bacteria which inhabit the particles and utilize the  $Fe^{2+}$  in the waste water as the energy source and at the same time to lower the  $Fe^{2+}$  content of the waste water;

15 transferring the treated suspension of the iron bacteria-bearing particles from the oxidation and culture zone to a sedimentation zone;

20 recovering the oxidized waste water containing  $Fe^{2+}$  in the sedimentation zone by precipitating to separate the particles from the treated suspension; and

returning the separated particles which the iron bacteria inhabit to the oxidation and culture zone.

25 The process of the present invention is applicable to any acidic waste water containing the  $Fe^{2+}$ , and is especially advantageous when applied to waste water having such a pH range as to provide little precipitation of the basic salts of the  $Fe^{3+}$ , for example of 2.0 or lower.

30 However, this invention is also applicable to such acidic

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range as of pH  $>2.0$  if the precipitated salts are separated or circulated.

"An acid-resistant, porous and particulate material" as used in the present invention means any porous material with a surface area great enough for a large number of iron bacteria to inhabit it, and possesses the properties of readily flowing when agitated and of immediately precipitating with or without addition of coagulant when allowed to stand. The inventors have found by experiments that particles of diatomaceous earth have these properties and are excellent as the porous material. For example, when acid-resistance, sedimentation by coagulation and/or flocculation and fluidity of the materials listed in Table 1 were examined, it was found that F-type diatomaceous earth is, especially effective when used in the present invention.

The test results of each of the diatomaceous earths of Types A-F in X-ray diffraction did not reflect the difference in constituent elements. But, as shown in Table 2, the measurements of specific surface area indicated that F-type diatomaceous earth is preferable as a bed material for iron bacteria since it has a large specific surface area and thus can maintain many bacteria adsorbed thereon.

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Table 1

Materials \ Items	Acid-resistance	Coagulation or flocculation and sedimentation	Fluidity
A-type diatomaceous earth	0*	0	X
B-type "	0	X	X
C-type "	0	X	X
D-type "	0	X	X
E-type "	X*	0	X
F-type "	0	0	0
Synthetic zeolite	0	0	X
Effloresced granite	0	0	X
Slate powder	0	0	X
Dressing 'slime'	X	0	X

\* 0 represents high, and X represents low.

Table 2

Materials \ Item	Specific surface area (cm <sup>2</sup> /g)
A-type diatomaceous earth	42128
B-type "	29605
C-type "	14341
D-type "	48481
E-type "	90347
F-type "	367242

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Embodiments of the present invention which continuously oxidize the  $Fe^{2+}$  in waste water by culturing iron bacteria in a densely populated state using as their bed an acid-resistant, porous and particulate material with such a large surface area as shown in Table 2 and utilizing the  $Fe^{2+}$  as the energy source will be illustrated with reference to the attached drawing. In the drawing, Figure 1 is a view of a circulation-type system divided by vertical partitions into several compartments suitable for use in carrying out the present invention; and Figure 2 is a view of an automatic circulation-type conical system used in carrying out the present invention.

In Figure 1, the circulation-type system is composed by separately disposing an oxidation tank 1 constituting an oxidation and culture zone, and positioning a liquid delivery pipe 3 for a suspension and a return pipe 4 for a porous particulate material between them.

In the oxidation tank, the acidic waste water which is introduced through a waste water inlet pipe 5 is oxidized by iron bacteria supported on particles of a porous material such as diatomaceous earth suspended and movable in the oxidation tank 1. That is, in the course of streaming through the tank divided into compartments by partitioning-boards 6 to a liquid delivery pipe 3, the waste water is contacted with diatomaceous earth which is circulated from the return pipe 4 and is subjected to oxidation treatment while keeping suspension conditions by blowing a stream of air into the water through an air pipe 7. The bacteria which inhabit the diatomaceous earth grow, utilizing the  $Fe^{2+}$  in the waste water as the energy source, until the

number of the bacteria reaches the maximum for the surface  
area of the diatomaceous earth. Accordingly, the larger  
the specific surface area of the porous particles, the  
easier the oxidation of the  $Fe^{2+}$  due to increase in the  
5 cell number of the bacteria on the particles. Thus, the  
cell number reaches its maximum in the waste water with  
bacteria adsorbed on the particles circulated through the  
return pipe 4 and those on fresh porous particles. On the  
other hand, the  $Fe^{2+}$  in the waste water is oxidized by the  
10 highly dense bacteria population and supplied to the next  
step almost in the form of  $Fe^{3+}$ .

The oxidized suspension, which flows through the  
liquid delivery pipe 3 into the sedimentation tank 2  
together with the porous particulate materials such as  
15 diatomaceous earth, is separated into solid and liquid  
phases in the sedimentation tank 2, and the diatomaceous  
earth precipitated at the bottom is circulated together  
with the cells adsorbed thereon through the return pipe 4  
to the upper part of the oxidation tank 1 by a pump 8.

20 The treated waste water, the  $Fe^{2+}$  content of which  
has decreased due to oxidation of almost all of the  $Fe^{2+}$   
to  $Fe^{3+}$ , is discharged from the upper part of the sedimen-  
tation tank and supplied for subsequent treatment such  
as neutralization, metal ion recovery and the like.

25 Figure 2 exemplifies a system which makes it possible  
to conduct an oxidation and culture step and a sedimentation  
step in one container. This system of Figure 2 is formed  
by disposing an inner pipe 10 in a reversed-conical con-  
tainer 9 without contact to provide an oxidation and culture  
30 zone (oxidation tank 1) therebetween, positioning further

an exterior pipe 11 around the inner pipe 10 to provide a coagulation and/or flocculation zone, and instituting a sedimentation zone (sedimentation tank 2) in the periphery of the exterior pipe 11.

5           A stream of waste water to be treated is injected into the oxidation tank 1 through a waste water inlet pipe 5 located at the upper part thereof, and a stream of air is blown into the tank 1 through an air pipe 7 located at the bottom thereof. By this, the porous particles of for  
10           example diatomaceous earth present in the oxidation tank 1 float, and as previously explained with reference to Figure 1 the formation of a dense bacteria population and the oxidation of the  $\text{Fe}^{2+}$  proceed at the same time. The oxidized suspension overflows over the top of the oxidation  
15           tank 1 into a flocculation zone 12. In this flocculation zone 12, the flocculation of the diatomaceous earth particles is facilitated for example with addition of a high-molecular coagulant(s) through its upper opening 13.  
A part of the flocculated diatomaceous earth precipitates  
20           and is sent to the oxidation tank 1 through the bottom slit of the inner pipe 10. The remaining diatomaceous earth particles go along with the waste water into the encircling sedimentation zone (sedimentation tank) 2 wherein there is no agitation action, and precipitate there. Then the  
25           particles are circulated into the oxidation tank 1 through the bottom slits of the inner pipe 10 and the exterior pipe 11, and the oxidized waste water from which the precipitated diatomaceous earth particles have been separated is recovered at 14.

30           Thus, even in the above automatic circulation-type

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conical system iron bacteria can make use of porous particles as their bed, and grow utilizing the  $Fe^{2+}$  in the waste water to be treated as the energy source; by this the cell population on the particles is always maintained at a saturated level, and thus the oxidation rate of the  $Fe^{2+}$  increases.

The system shown in Figure 3 has the same function as that illustrated in Figure 2, and is modified to provide a flat plane at the bottom to improve execution and structure. The reference numbers in Figure 3 have the same meaning as do the corresponding numbers in Figure 2.

The present process may be applied to a batch-wise operation in factories discharging a minor amount of waste water at a lower pH; the waste water is stored in a tank for a predetermined number of days, then streams into an oxidation tank wherein iron bacteria are cultured, and is air-blown for a predetermined period of time to oxidize the  $Fe^{2+}$  to  $Fe^{3+}$ . After complete oxidation, the air-supplying is stopped and the precipitate is separated to give a supernatant containing the  $Fe^{3+}$ .

The following example is an illustration of the present invention using the automatic-circulation type conical system as shown in Figure 2.

### Example

A stream of an acidic mine effluent was supplied into a system of 300 liter capacity as shown in Figure 2 at a rate of 5 l/min. for 50 days. Particles of diatomaceous earth (6 w/v%; specifically, F-type diatomaceous earth in Table 1) have been added to, and a stream of air of 80 l/min. has been blown through the air pipe 7 into

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the oxidation tank 1. The properties of the mine effluent to be treated are tabulated in Table 3 which includes the maximum and minimum values of valuables such as the temperature, pH and components content of the waste water fed to the system during the fifty-day run.

5

Table 3

Temperature of waste water ( $^{\circ}\text{C}$ )	2 - 20
Mean cell number (per ml)	$25 \times 10^4$
pH	1.5 - 1.60
Total Fe (mg/l)	876 - 1040
Fe <sup>2+</sup> (mg/l)	856 - 1010
Al (mg/l)	200 - 250
SO <sub>3</sub> (mg/l)	4000 - 5000



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Table 4

Days	Fe <sup>2+</sup> content of mine effluent before oxidation (mg/L)	Fe <sup>2+</sup> content of oxidized mine effluent (mg/L)	Oxidation rate	Remark
1	966	966	0	Batch-wise oxidation
2	"	961	0.5	
3	"	956	1.0	
4	"	952	1.5	
5	"	930	3.7	
6	"	887	8.2	
7	"	792	18.0	
8	"	464	52.0	
9	1010	334	66.9	Two hour continuous oxidation
10	966	146	84.9	One hour continuous oxidation
11	"	168	82.6	
12	"	144	85.1	
13	"	114	88.2	
14	955	72	92.5	
15	966	49	94.9	
16	955	43	95.5	
17	966	41	95.8	
18	955	52	96.6	
19	944	30	96.8	
20	955	31	96.8	
21	944	27	97.1	
22	"	"	"	
23	"	25	97.3	
24	"	24	97.5	
25	"	"	"	

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Days	Fe <sup>2+</sup> content of mine effluent before oxidation (mg/L)	Fe <sup>2+</sup> content of oxidized mine effluent (mg/L)	Oxidation rate	Remark
26	933	23	97.5	One hour continuous oxidation
27	"	"	"	
28	955	24	"	
29	944	22	97.7	
30	933	21	"	
31	"	15	98.4	
32	"	"	"	
33	944	"	"	
34	933	14	98.5	
35	"	"	"	
36	922	"	"	
37	900	"	"	
38	"	"	"	
39	888	13	"	
40	"	"	"	
41	880	12	98.6	
42	"	"	"	
43	868	10	98.8	
44	"	"	98.9	
45	"	"	"	
46	856	9	99.0	
47	"	8	99.1	
48	"	"	"	
49	"	"	"	
50	"	"	"	

The  $\text{Fe}^{2+}$  content of the waste water before and after treatment according to the present invention was measured everyday during the fifty-day treatment and the oxidation rate of the  $\text{Fe}^{2+}$  was calculated. The result is shown in  
5 Table 4.

The above result shows that the iron bacteria in the waste water to be treated reach the diatomaceous earth bed and grow thereon, and in about ten days the bed becomes saturated with the bacteria, and later this saturation is  
10 kept, which enables to maintain the reduced  $\text{Fe}^{2+}$  content of the oxidized water to ensure increased oxidation rate of almost 100%.

With full regard to the fact that the generation of ordinary iron bacteria seems to be about 20 hours,  
15 continuous culture of iron bacteria in a diatomaceous earth bed provides conditions extremely effective for oxidation of the  $\text{Fe}^{2+}$  in waste water.

In addition to the result given in Table 4, the temperature change in the oxidation tank is represented  
20 graphically in Figure 4. Figure 4 indicates that almost 100% of oxidation rate is obtained independently of the temperature change if the diatomaceous earth bed is saturated with iron bacteria.

As is clear from the above-mentioned, the process  
25 of the present invention provides continuous oxidation of  $\text{Fe}^{2+}$  with a rate of almost 100% effectiveness. Further advantages of the process of the present invention as compared with the prior art processes are as given below:

(1) In contrast to conventional process based on  
30 liquid-culture, the cell content in the oxidation zone is

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not reduced, but is increased to raise the cell number per unit amount of the waste water to be treated. Accordingly, it is possible to obtain a high oxidation rate even in treating a large amount of waste water;

5           (2) For the same reason as the above, the present process is operable in a relatively low temperature range in view of the existing established theory on the temperature conditions, and thus effective oxidation is possible even at extremely low temperatures; whereas "the existing  
10 established theory on the temperature conditions" is that the oxidation rate (amount) suddenly drops at temperatures below 20°C, and "extremely low temperatures" are the lowest temperatures within the range in which the waste water to be treated does not freeze;

15           (3) By the use of anti-acid porous particles, the present invention may be applied to the waste water the pH of which is lower than 2.0; and

            (4) Separate culture equipment is not necessary, and the culture is possible in the waste water treatment  
20 plant according to the present invention.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the oxidation with iron bacteria of the ferrous ions ( $\text{Fe}^{2+}$ ) contained in mine and other similar factory effluents at a pH of 2.0 or lower to provide little precipitation of basic salts, characterized by the following steps:

passing the stream of waste water, at said pH, to be treated to an oxidation and culture zone which includes a bed of a particulate material consisting essentially of an acid-resistant, porous and particulate material having a specific surface area of from about 14,000 to about 370,000  $\text{cm}^2/\text{g}$  for the iron bacteria;

oxidizing the ferrous ions ( $\text{Fe}^{2+}$ ) by agitating and blowing air into the waste water with said particles suspended therein to culture the iron bacteria which inhabit the particles and utilize the ferrous ions ( $\text{Fe}^{2+}$ ) in the waste water as the energy source and at the same time to lower the ferrous ions ( $\text{Fe}^{2+}$ ) content of the waste water;

transferring the treated suspension of the iron bacteria-bearing particles from the oxidation and culture zone to a sedimentation zone;

recovering the ferric ions ( $\text{Fe}^{3+}$ )-containing oxidized waste water in the sedimentation zone by precipitation to separate the particles from the treated suspension; and

returning the separated particles which the iron bacteria inhabit to the oxidation and culture zone.

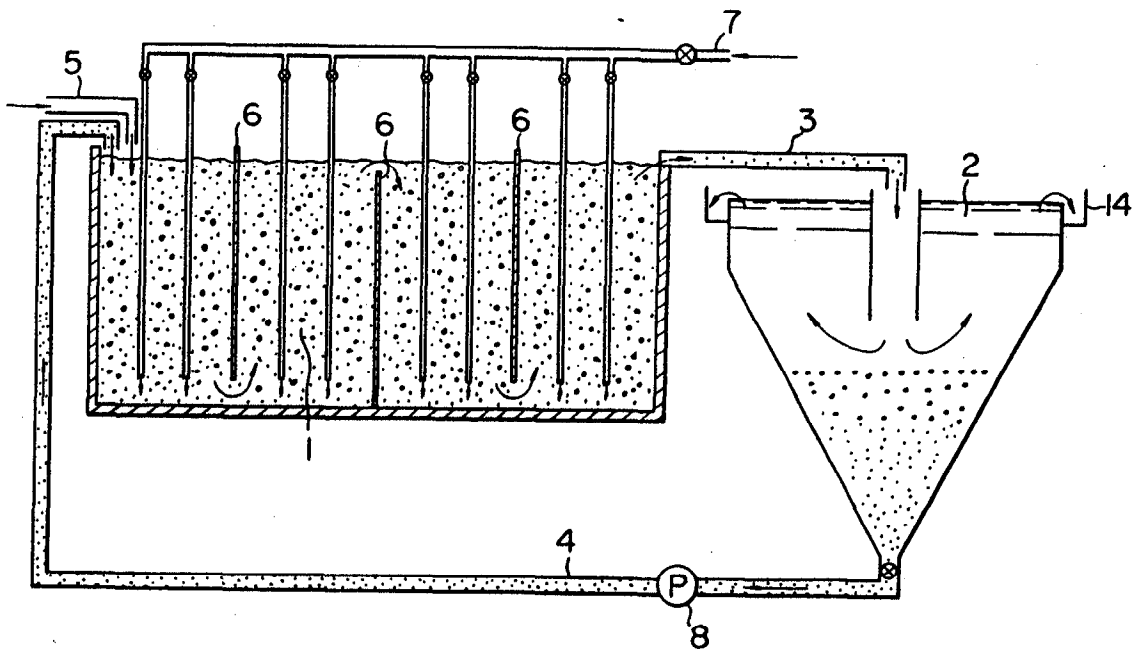
2. The process of Claim 1, wherein the said particulate material is a diatomaceous earth.

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3. The process of Claim 1, wherein the said particulate material is F-type diatomaceous earth having a specific surface area of about 370,000 cm<sup>2</sup>/g.



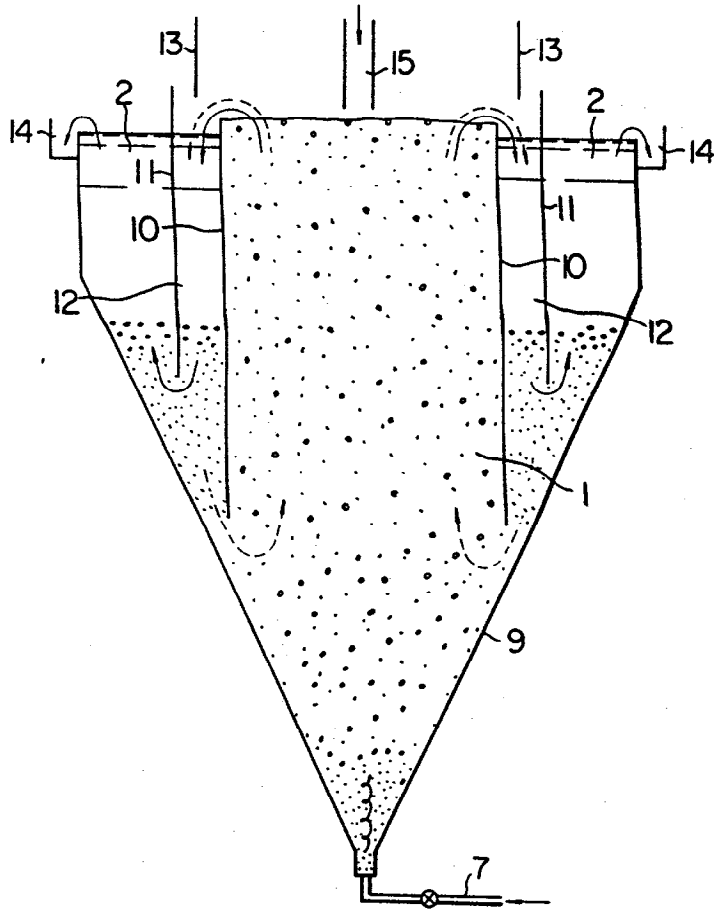
Fig. 1



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Fig. 2

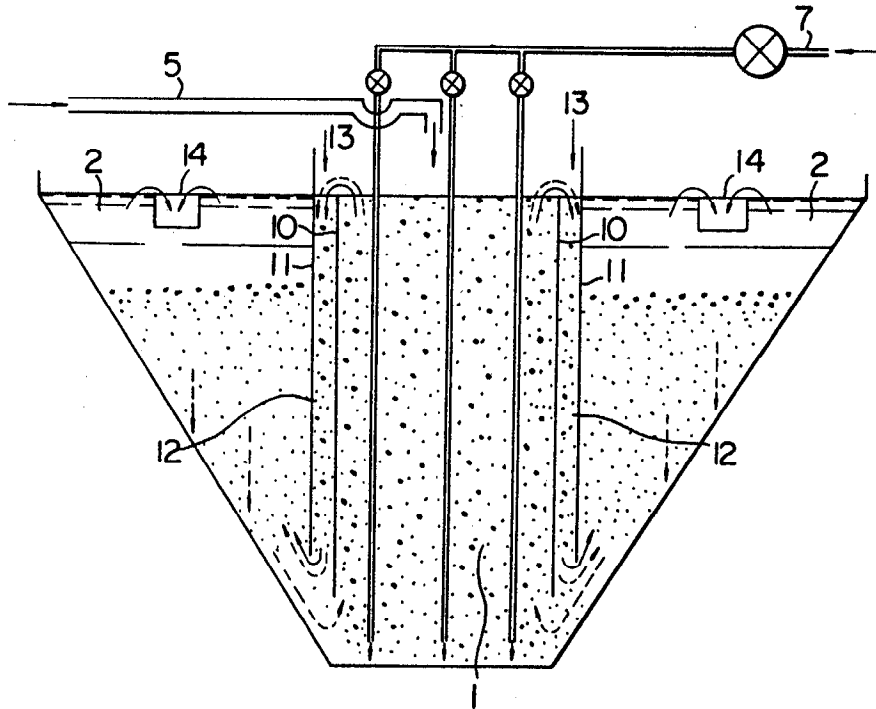


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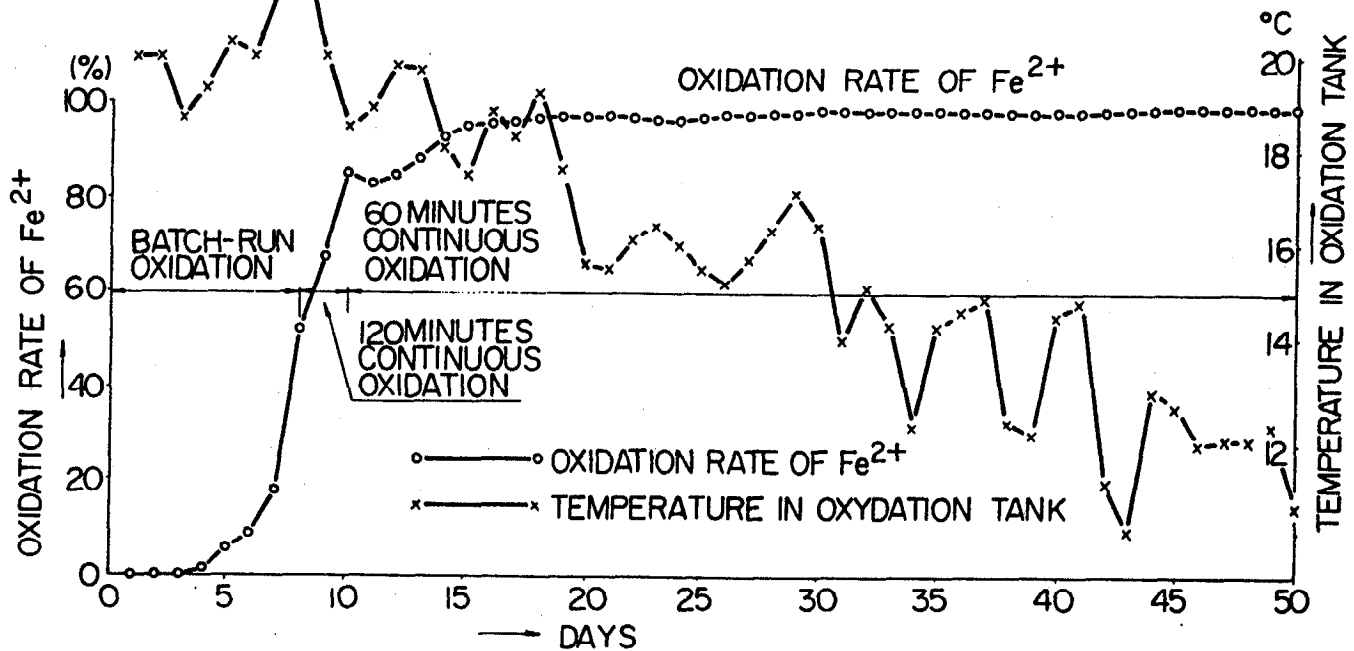
Fig. 3



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Fig. 4



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