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CLAY TAILINGS FROM ALBERTA OIL SANDS
AND OTHER SOURCES. A REVIEW

Prepared by
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CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
EXECUTIVE OUTLINE	v
INTRODUCTION	1
OIL SANDS EXTRACTION	
Occurrence and Development of Deposits	3
Environmental Considerations	5
Tailings Disposal	9
HOT WATER PROCESS CLAY TAILINGS	
Origin of Clay Tailings	13
Composition	19
Microbial Population	22
Flocculation and Sedimentation	26
Sludge Dewatering and Disposal	29
Materials Recovery from Tailings	31
Reduction by Process Modification	33
TAILINGS FROM OIL SANDS EXTRACTION PROCEDURES OTHER THAN THE HOT WATER PROCESS	
General Comments	35
Sand Reduction Methods	36
Cold Water and Solvent Extraction Processes	38
Direct Coking	40
In Situ Recovery	41
CLAY TAILINGS FROM OTHER EXTRACTIVE INDUSTRIES	
Bauxite Mine Tailings	43
China Clay Tailings	46
Diamond Mine Tailings	48
Phosphate Mine Tailings	49

	<u>Page</u>
CONCLUSIONS AND RECOMMENDATIONS	55
APPENDIX	
Clay Structures	59
Clay Interactions with other Materials	64
Characteristics of Clay Flocs	69
Drilling Muds	70
REFERENCES	73
Figure 1.	
Typical Arrangement of Oil Sand Particles	15
Figure 2.	
Flow Diagram of the Primary Extraction Process	16
Figure 3.	
T and O Sheets in Clay Structures	61
Figure 4.	
Clay Structures	62

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ABSTRACT

Data in existence in the open literature or in unclassified company reports on the physical, chemical and microbiological characteristics of Alberta's oil sands clay tailings are reviewed. Treatment and disposal procedures for these tailings, as well as for clay tailings from other industries, are discussed. Tailings disposal requirements, particularly those of an environmental nature, are appraised for in-situ and other oil sands bitumen recovery operations currently being considered as alternatives to the hot water process for mineable deposits. General background to the disposal problems is provided in brief descriptions of the extractive processes involved, as well as in an Appendix summarizing the structure and properties of clay minerals.

EXECUTIVE OUTLINE

The satisfactory disposal and abandonment of clay slimes resulting from the hot water extraction of surface-mined Athabasca oil sands is necessary for continued large scale application of this process. The current slime inventory in the GCOS settling pond and that projected to derive from the Syncrude operation present significant problems in this regard. Although it is likely that technological developments will eliminate or significantly reduce the production of clay slimes during surface-mined oil sand extraction, it is also likely that as a result of the inherent lag in implementing new technology, other conventional hot water plants will be constructed which too will produce massive amounts of bituminous slimes in the interim.

Information contained in the open literature (including non-confidential government and company reports), on research and development on the composition, handling, and disposal of oil sands clay slimes, has been surveyed. Similar information for the four other major industries that produce clay slimes; bauxite purification (North America and Australia), China clay mining (U.K.), diamond mining (South Africa), and phosphate mining (Florida), has also been reviewed.

The clay tailings produced by hot water oil sands extraction and by these other industries present a common problem. Although the clay will settle from these tailings in conventional sedimentation ponds to provide at least some water for recycle, the resulting clay sludge, or slime, is still too fluid to be used for backfill and its storage above ground in dyked-off areas poses a hazard to the surrounding habitat. The fluidity is a result of the physical properties of the clays in the tailings, and much effort has been expended in developing ways to dewater the slimes, both to provide more recycle water and to thicken the slimes to the point where they can be stored in a stable configuration. There is considerable overlap between the above industries in this endeavour.

The Florida phosphate industry, which has existed since the end of the last century, has produced to date about 50,000 acres of slimes, 40 to 60 feet deep. Most of this slime is currently stored above ground behind dykes, of which 30 have failed since 1940. The industry is currently suffering considerable adverse publicity. Stringent requirements have been placed on the companies involved and a combined research effort to solve the clay slimes

disposal problem, involving industry, government and universities, has been functioning since 1972. Much of the work reported in the context of oil sands tailings has thus already been investigated by the Florida phosphate mining industry. It is recommended that some of the newer techniques under investigation in Florida also be evaluated in the context of the tar sands situation. Of particular interest might be slime containment in mined-out areas, with crust formation as a precursor to revegetation or use as a stable lake-bed, sandwich placement of alternate sand and clay tailings in mined-out areas, sand-spray into slime disposal areas to aid dewatering, and repulping of settled slimes with sand prior to final disposal.

Some of the major processes that have been suggested as alternative to hot water extraction of mined deposits are discussed in the text and their potential for tailings production evaluated. It is concluded that in all cases the production of clay slimes should either be eliminated or significantly reduced. Indeed, this has been a major incentive for developing these alternate methods. In the case of in situ extraction, the amount of clay that would be brought to the surface is uncertain, but in any case would be considerably less than that produced by the hot water process. If it is significant in quantity, however, it would have to be separated from the process stream and stored above ground, since no mined-out areas would be available.

Many dewatering techniques, although prohibitively expensive for massive volumes of clay slimes, may be useful in the treatment of the smaller quantities either produced by in situ operations or involved in crust formation over large accumulations. It is recommended that investigation of dewatering techniques be carried out for these applications only. Flocculation studies should also be pursued in the sense of providing a more readily dewaterable sludge, and not from the point of view of clarification.

Potential bacterial metabolism of bitumen constituents within oil sands tailings ponds is a matter of concern, in that it could yield undesirable components which may gain entry to nearby receiving waters through dyke drainage. On the other hand, if bacterial metabolism is amplified using activated sludge processes, undesirable constituents within tailings pond drainage, perhaps combined with upgrading plant effluents, might well be reduced or eliminated. To date there has been no consistent monitoring of microbial viable counts, either within the existing G.C.O.S. tailings pond, or within discharges from the dyke or

the upgrading plant. Such monitoring is a prerequisite to any further consideration of these possibilities.

INTRODUCTION

The only method currently used for the commercial separation of bitumen from surface-mined oil sands is based on the Clark hot water extraction process. After a series of set-backs and technical difficulties, the Great Canadian Oil Sands (GCOS) hot water plant is now operating consistently. The Syncrude hot water plant is scheduled to start up in 1978. The latter is designed to produce some 123,000 barrels of synthetic crude oil per day, which is approximately double the output of the pioneer GCOS facility.

A major concern still remaining with the large-scale application of hot water extraction is the production of clay slimes. Although it was recognized as far back as 1953 that extraction of surface mined oil sands by any of the processes then being considered (hot water, cold water or fluidization) would result in a massive accumulation of tailings, the problem that would be caused by the clay fraction of these tailings was not fully anticipated. It was assumed that the clay tailings would settle, much as tailings from other mining ventures, to provide recycle water, and eventually form a compact sludge which would present no major problems for abandonment and revegetation. This has not proven to be the case. Apparently as a result of the properties of the clays involved, simple settling will not produce a sludge beyond a clay to water weight ratio of about 0.24. Consequently, the GCOS settling pond is now in reality a very large storage area, with the accumulating volume of sludge requiring continuous elevation of the dyke to contain it.

The settled clay sludge is still liquid and constitutes a real threat to waterways in the area, should dyke failure occur. Since the storage area is adjacent to the Athabasca River, this watercourse would immediately be affected, followed by Lake Athabasca itself. More mobile constituents of the tailings, such as trace metals, hydrocarbons and fines would probably find their way throughout a large part of the Mackenzie River drainage basin. There is evidence that some of these more mobile constituents would be acutely toxic towards fish. Some components may also prove chronically toxic and constitute a threat if they become incorporated in food chains following sudden release or even seepage from dyked areas. In addition, a massive release of tailings would almost certainly cause flooding and fouling

of surrounding land areas.

Although the Syncrude design includes a much larger settling and impoundment area for the clay slimes well away from the Athabasca River, these will nevertheless be stored above grade and will still present some threat to nearby waterways and adjoining land areas, including the mining sites themselves. Slime disposal areas also will become inaccessible to wild life, for several decades at least. The unmodified sludge surface cannot support the weight of land animals, and its surface and dissolved hydrocarbon contents will probably prevent habitation of the area by water-fowl and fish, and the establishment of aquatic plants, until such time as the hydrocarbons are removed by microbial activity or physical mechanisms. While this situation may be tolerable for a low level of development, it would become unacceptable if the clay disposal areas were to approach the size of those currently existing in Florida as a result of phosphate mining operations.

It is very likely that extraction techniques will be developed for surface mined deposits that considerably reduce or eliminate liquid tailings ponds. In the interim, however, a large volume of slimes already exists, and methods for its ultimate stabilization are still uncertain. A large volume of slimes will be produced by the Syncrude plant, and there is the distinct possibility that as a result of the time lag inherent in developing new technology, further hot water process plants will be constructed, which will generate more slimes. This report is therefore designed to provide an information base for research in the area of oil sands clay tailings treatment.

Clay disposal problems in other extractive industries, such as that of phosphate mining in Florida, are discussed in the report. Whenever possible, experiences in these industries which have bearing on the situation in Alberta are cross-referenced by page number.

OIL SANDS EXTRACTION

Occurrence and Development of Deposits

According to Walters (1974) the major accumulations of oil sands are restricted geographically to 8 countries of the world. Over 95% of the known in-place oil volumes occur in Canada (894×10^9 bbl), Venezuela (700×10^9 bbl) and to a lesser extent, the U.S. (29×10^9 bbl). Other countries in which significant deposits occur are Trinidad (60×10^6 bbl), Madagascar (1.75×10^9 bbl), Albania (unknown), U.S.S.R. (of the order of billions bbl), and Rumania (25×10^6 bbl). Minor deposits, less than 1 million barrels, occur in Spain, Portugal, Cuba, Peru, Argentina, Kuwait, Thailand, Phillipines and Senegal, as well as a deposit of unknown size in Columbia.

To this date, only the Athabasca oil sands in Canada have been exploited on a commercial basis, using the hot water extraction process, although there has been some interest in developing the U.S. and Venezuelan deposits. Sepulveda (1976) reports on the possible use of a hot water process with respect to the U.S. deposits in Utah. These oil sands appear to be structurally dissimilar to those in the Athabasca region in their water and clay content, and hence the tailings would be expected to be of a different nature. Processes here have not yet progressed to the point where tailings characteristics and methods for disposal have been considered. Representatives from Venezuela, the U.S. and Canada have recently participated in a joint conference on oil sands technology in Edmonton (CIM, 1977).

Camp (1976) provides an excellent introduction to all aspects of the Alberta Oil Sands in a monograph now published in its third edition. Bowman (1967) has discussed the molecular and interfacial properties of tar sands that have direct bearing on the selection of extractive methods. A review of such methods applied to the Alberta Oil Sands is provided by Berkowitz and Speight (1975). Hot water extraction is now considered established technology, with considerable research progressing on in situ methods of recovery.

Early attempts to develop the oil sands by Abasand Oil Limited are described in an article by Ball (1941), and reviews of the Great Canadian Oil Sands operation have been provided by Allen (1974, 1976) and Humphreys

(1973). Gray (1974, 1976) has published a series of articles describing the Syncrude project.

A brief review of in situ recovery methods that have shown promise in field testing is given by Redford (1976). Included in the review are methods involving formation pre-heating and wet-forward combustion, single well steam stimulation and interwell vertical steam drive and steam stimulation. Also included is a description of current research using physical simulators. In situ projects currently in pilot stage are being carried out by Amoco at Gregoire Lake, Imperial Oil at Cold Lake and Texaco at Fort McMurray. Their potential is discussed in comparison with mining processes (Oilweek, 1976).

The Alberta Oil Sands Story, issued in 1974 by the Alberta Department of Federal and Intergovernmental Affairs, considers the future role of Alberta's oil sands in meeting Canada's energy requirements. Economic and demographic projections are discussed in the report in terms of a possible 20 to 30 recovery plants with capacities of 100,000 - 150,000 bbl per day, with a construction rate of 1 plant per year between 1980 and 2000. Baugh and McClennon (1976) also present an economic analysis of the future of oil sands mining. Although they point out that development of further oilsands projects following Syncrude has ground to a virtual stop, they assume that increasing world oil prices will eventually lead to an aggressive development program. Reasons for the pause in oil sands development are also considered in an article by Dalby (1976). A general synopsis on the future of oil sands development, both mining and in situ, is given by Carrigy (1974). The companies and consortiums that have shelved plans for extraction plants due to a variety of political and economical reasons include Shell Canada Ltd. (both in situ recovery and hot water extraction of mined deposits, applications withdrawn 1968 and 1976 respectively), Home Oil Co. Ltd. and Alminex (hot water process, withdrawn 1970), Amoco Canada Ltd. (in situ COFCAW, withdrawn 1970), and the AOP group (hot water extraction, withdrawn 1976).

Environmental Considerations

The Government of Alberta has commissioned several reports on the oil sands and the impact of their development as a natural resource. "An Environmental Study of the Athabasca Oil Sands" was completed by Intercontinental Engineering of Alberta for the provincial government in March 1973, and dealt in some detail with a variety of environmental components and conditions of the area, biological, human and physical. Adverse effects on these of a number of human activities were considered. Such activities included exploration, plant construction, preparation for surface mining, overburden stripping, blasting, surface mining, hot water extraction, tailings placement, reclamation, bitumen processing, utilities plant locations and size, in situ recovery, and direct coking.

A report outlining the requirements regarding the environmental impact of tar sands development has also been published by the Alberta Department of Environment (1973). Syncrude Canada Ltd. has issued brochures (1973, 1974) describing how the company foresees its mining activities affecting the environment. The company has also published a 4 vol. Environmental Impact Assessment (1973), in which details are provided on the projected growth of the clay tailings pond over the years of operation of the extraction plant. There are no plans presented in the Assessment for the further stabilization of the dyked-off slimes on abandonment of the site.

Much environmental concern with the oil sands projects has centered on SO₂ emissions (Northern Environmental Consultants, 1975; Can. Envir. Law News, 1975; Ottawa Report, 1976; GCOS News Release, 1976). The report, "Evolution of Pollution Abatement Technology as Applied to the Alberta Oil Sands", Western Research and Development Ltd. (1976) deals almost exclusively with air pollution problems associated with the high sulfur content of the Athabasca bitumen.

Noticeable introduction of oil to the Athabasca River from the GCOS plant has resulted from sources other than the tailings pond, such as pipe ruptures (Env. Health Services Rept., 1970). The river has recovered quickly in these instances, and in fact oil, which finds its way into the river from seams along the banks, has been accommodated by natural means for

millenia.

A recent article in Canadian Petroleum (1974) asserts that a major problem with hot water extraction methods for surface mined oil sands is the need for tremendous volumes of water. The article points out that the Great Canadian Oil Sands plant was then using 10 million gallons of water for every 100,000 tons of oil sands processed. If large scale processing of mined oil sands were to be carried out with current methods, the article suggests, there may be neither enough water nor enough storage area for spent water. Shewchuk (1974) in a report issued by the Standards and Approvals Division of the Department of Environment considers the projected water requirements and waste water management systems of oil sands recovery plants. He calculates that the consumptive use of water from the Athabasca River for a production level of 10^6 barrels per calendar day of synthetic crude oil, using surface mining techniques and the Clark hot water separation process, would amount to 350 cubic feet per second, or approximately 10% of the minimum monthly average flow of the Athabasca River. The waste water management concept used in arriving at these figures involves impounding all water in perpetuity and maximizing the re-use of process waste waters originating from the mining pit area, the extraction and bitumen upgrading plants and the utilities plants as well as plant site surface run-off. Tailings ponds are projected to range from 6 to 10 square miles in area per plant.

Water requirements for an in situ recovery process based on steam injection are also briefly discussed. Such a system capable of 10^6 BPCD is expected to use 362 cfs of water in order to displace about 60% of the bitumen in place and for process demands. Transport of the bitumen to the surface would be in the form of an emulsion, from which maximum water recovery is assumed. Water management for the hot water process in toto, where bitumen recovery is balanced with other considerations, such as water usage, is the subject of a patent issued to Camp and Baillie (1972).

Reclamation has only been attempted so far on tailings dykes and overburden waste dumps, primarily to provide a degree of stabilization. Much has been published on vegetation methods in these contexts (see for instance Berry et al, 1974; Lulman, 1974; Allen, 1976; Massey, 1970, 1972). The first Annual Report of the Alberta Oil Sands Environmental Research

Program (1975) also describes ongoing projects in the revegetation of disturbed areas.

Attempts to reclaim oil sands clay tailings disposal ponds have not yet been carried out and as yet do not appear to be planned. Tailings disposal in general was recognized as a problem by Djingheuzian in 1953. While working on the development of the cold water process, he calculated that the processing of one cubic yard of plant feed would produce up to 1.4 tons of waste, or approximately 1.24 cu. yds., resulting in a net increase in volume. Very similar figures have in fact been realized during the commercial operation of the hot water process (Camp, 1976). A four-company team of U.S. and Canadian oil companies, Cities Services Athabasca Inc., operator, Imperial Oil Ltd., Richfield Oil Corp., and Royalite Oil Co. Ltd. appeared before the Alberta Oil and Gas Conservation Board in 1960 in opposition to the Great Canadian Oil Sands Ltd. application to develop the 4,000 acre lease adjoining the group's acreage. They cited, amongst other reasons, problems associated with tailings disposal (Petroleum Week, 1960).

It is probable that neither this consortium, nor Djingheuzian, realized the full significance of the clay problem, however. This problem is best defined by a statement on tailings and sludge disposal issued by Great Canadian Oil Sands Limited in 1974. It is quoted verbatim as follows:

"The tailings from the hot water extraction process consists of a slurry of sand, silt, clay and about 1% bitumen in water at a pH of 8.3 and temperature of 120° F. The coarse sand settles out to form the dykes of the tailings pond. The fine material in the pond settles slowly and at a decreasing rate until a concentration is reached at which the rate of settlement is essentially zero. Two layers are formed in the pond. The upper layer containing less than 5% solids is reusable in the plant. The lower "sludge" layer containing 5-30% solids is not reusable and is a net accumulation which has proven extremely difficult to separate into solid and water components. The total net volume of the tailings (sand plus sludge) is 40% greater in volume than the mined tar sand thus presenting a serious backfill problem.

A solution to the problem should meet the following criteria:

1. Recovered water from the "sludge" should be suitable for either reuse in the plant or return to the river.

2. Recovered solids from the "sludge" should meet backfill requirements, i.e. compactability, non-leachability, etc.
3. Costs must be reasonable. Less than \$1.00 per 1000 Imperial gallons of "sludge" is considered reasonable. "

Tailings Disposal

Most discussions of tailings disposal and the construction of tailings ponds has centred around the base metal mining industry, and many of the procedures and configurations used in this regard are applicable to the disposal of clay tailings. The industries that produce large quantities of clay tailings are few in number, and are discussed individually in a later section. Clark (1973) discusses the problems presented by the disposal of clay slimes. He suggests that although they present an increasing environmental problem, they present an opportunity for the recovery of values in that new technologies of mineral concentration in the 0.5-5 μ range, largely developed for the purification of clay minerals, allow the recovery of values as ends in themselves.

Bell (1974, 1975) discusses the use of tailings ponds, or modified systems based thereon, as the most common form of treatment for base metal mine and milling wastes. He also briefly considers alternative approaches, such as offshore marine disposal, disposal in deep lakes, use as backfill in the mine and processing for secondary values. Some typical schemes for the handling of mine tailings are also described in a report issued by the United States Environmental Protection Agency (1973).

Dean (1973) reviews the magnitude of mine-waste disposal problems, and describes related chemical and vegetative stabilization techniques. The costs of the various procedures are compared. Shirts (1976) has discussed the stabilization of tailings under widely varying climatic conditions, as well as the effect of the physical and chemical characteristics of the tailings themselves on the choice of stabilization procedures. The paper is concerned mainly with the magnitude of the problems associated with milling plant wastes.

Shields (1975) considers two methods of tailings disposal which depart from traditional designs, namely down-valley discharge from a cross-valley dam, and central discharge (leading to the build-up of a tailings cone). Robinsky (1975) discusses the central discharge concept at length. He suggests that this tailings disposal configuration eliminates the need for a decant system, along with its towers and lines with all the potential hazards of collapse, piping failure and washouts. In the system, tailings, previously thickened to 35-60% solids, are deposited in a cone-shaped hill in a disposal area surrounded by

low perimeter dykes. He points out also that the cone is a most stable configuration, that runoff is rapid and that penetration and leaching of the deposit is minimal, and that abandonment is simple, with the perimeter dykes being spread up onto the cone prior to reclamation. Mrost (1974) summarizes the soil mechanics, civil engineering and environmental considerations applicable to the construction of slimes dams on the Witwatersrand gold mines.

The possibility of combining mine tailings with domestic wastes prior to treatment in a holding lagoon is considered by Matthew (1972). In the specific instance discussed, the combined treatment configuration proved to be the most satisfactory, although it presented several design problems.

Duncan (1972) addresses problems caused by the water soluble components of tailings, such as cyanides, acids, xanthates, oils and various other organics, and heavy metals. The various techniques developed for abatement of pollution problems caused by these components are described in the review, which contains 66 references.

Mittal (1975) points out that tailings dams differ from conventional earth fill structures in that much more time is available to optimize design since their construction is over an extended period of time. He also presents data on a variety of tailings sands which indicate that they are relatively strong and incompressible, and suggests that poor performance is likely to result from inadequate seepage control and instability due to liquefaction. He describes a technique for carrying out in situ density determinations by using a radioactive probe driven into the sands, which he considers to offer considerable promise for evaluating the liquefaction potential of natural and fill deposits. Hardy (1974) discusses the construction of the tailings ponds on GCOS lease 86 and Syncrude lease 17 in the Athabasca Tar Sands region.

In 1975 Alberta Environment appointed a Design Review Panel to consider all the factors affecting the stability of the GCOS tailings dyke at Tar Island. The report (Alberta Environment, 1977) concludes that the dyke at present has an overall level of safety with regard to both foundation and embankment performance. Specific recommendations are made to ensure continuing safety and stability.

D'Appolonia (1972) points out that tailings facilities are often planned and operated to solve immediate problems associated with the disposal

of solids or clarification of process water, and that minor consideration is usually only given to the use of the facilities on abandonment. He suggests, however, that

"abandonment will no longer be a neglected item, nor one to be considered at the end of the operating life of the plant. Plans for abandonment will have to be developed during the feasibility stage of a project and will be submitted with the applicant's first request for a permit. Implementation for abandonment with allocated funds to assure a satisfactory, safe shutdown of a facility will have to be demonstrated."

In order to optimize the cost of waste handling and disposal, he proposes that

"alternatives for site preparation, operation and abandonment should be critically evaluated as an environmental, technical and economical multi-disciplined system."

GCOS, in 1972, recognizing that the combined volume of the sand and clay tailings produced by their process exceeded the volume of mined-out areas available for their disposal, requested that the Energy Resources Conservation Board accept a further amendment to their original scheme (Approval No. 540) to allow them to use additional storage area. The material to be transferred to the storage area would be drawn from deep in the existing tailings pond, and would have an approximate composition of 1.8% bitumen, 27.4% minerals and 70.8% water. The material is expected to remain as an unconsolidated slurry indefinitely. It is pointed out, however, that it could be moved at any time should it eventually become attractive to mine the underlying deposits, development of which is currently considered to be uneconomical.

Camp (1976) has recently reviewed the GCOS experiences with tailings disposal. A materials balance for the hot water extraction process is discussed, as well as the rate of accumulation of tailings and the characteristics of the tailings ponds. He defines the "pondwater problem" as being "to devise long term economically and ecologically acceptable means to eliminate, minimize, or permanently dispose of, the accumulation of liquid tailings or sludge". To this end, he considers that prospects for reaching a long term solution may be grouped into three categories:

- (1) Reduce sludge accumulation
- (2) Treat sludge after it is formed
- (3) Permanently impound sludge.

Each of these categories receives limited discussion in the light of GCOS operations and research. Dyke storage followed eventually by placement of settled tailings in mined out areas is considered in the projected Shell development (Shell Canada, 1975). Hendry (1974) suggests a sequence of overburden and tailings placement in and around areas mined out by draglines which would maximize land reclamation.

HOT WATER PROCESS CLAY TAILINGS

Origin of Clay Tailings

In order to follow the production of the clay slimes in the hot water process, some notes on the structure of the sands themselves, and a summary discussion of the GCOS operation through the extraction stage, are given below. The former is abstracted essentially from an article by Camp (1976) and the latter from that by Allen and Sanford (1974). The Syncrude extraction process is very similar to that of GCOS, and a brief description may be found in the most recent article by Gray (1976).

Athabasca Oil Sand is basically a mixture of bitumen, mineral, and water. Figure (1) is a schematic representation showing the general arrangement of the components. The bitumen content is variable, averaging 12 wt. % of the deposit, but ranging from zero to 18 wt. %. Water typically runs 3% to 6% of the mixture, increasing as bitumen content decreases. The mineral content, predominantly quartz, is relatively constant, ranging from 84% to 86%. The most important feature of this structure is assumed to be the water-wet nature of the sand particles. No direct confirmation of this structural picture has been published, although compelling indirect evidence is provided by the fact that most Athabasca tar sands are readily extracted by the hot water process. The existence of any substantial amount of fine material suspended in the water layer surrounding sand grains must be regarded as speculative. (For a typical sand grain of 100μ diameter, the water film thickness is believed to be on the order of 2μ , and the bitumen film thickness is $5-6\mu$. A substantial amount of the tar sand fines exceed these dimensions.) Large and variable amounts of clay are occluded in the formation in the form of thin and discontinuous beds as well as bands varying from 1 inch to an occasional 6 feet in thickness.

Prior to mining the sands, muskeg, and then overburden, must be removed from the site. The muskeg must be thoroughly drained before removal is possible. This is achieved by digging an extensive network of ditches, and allowing the muskeg to drain naturally for two years. Despite the extended drainage period, muskeg will remain spongy and wet and must be

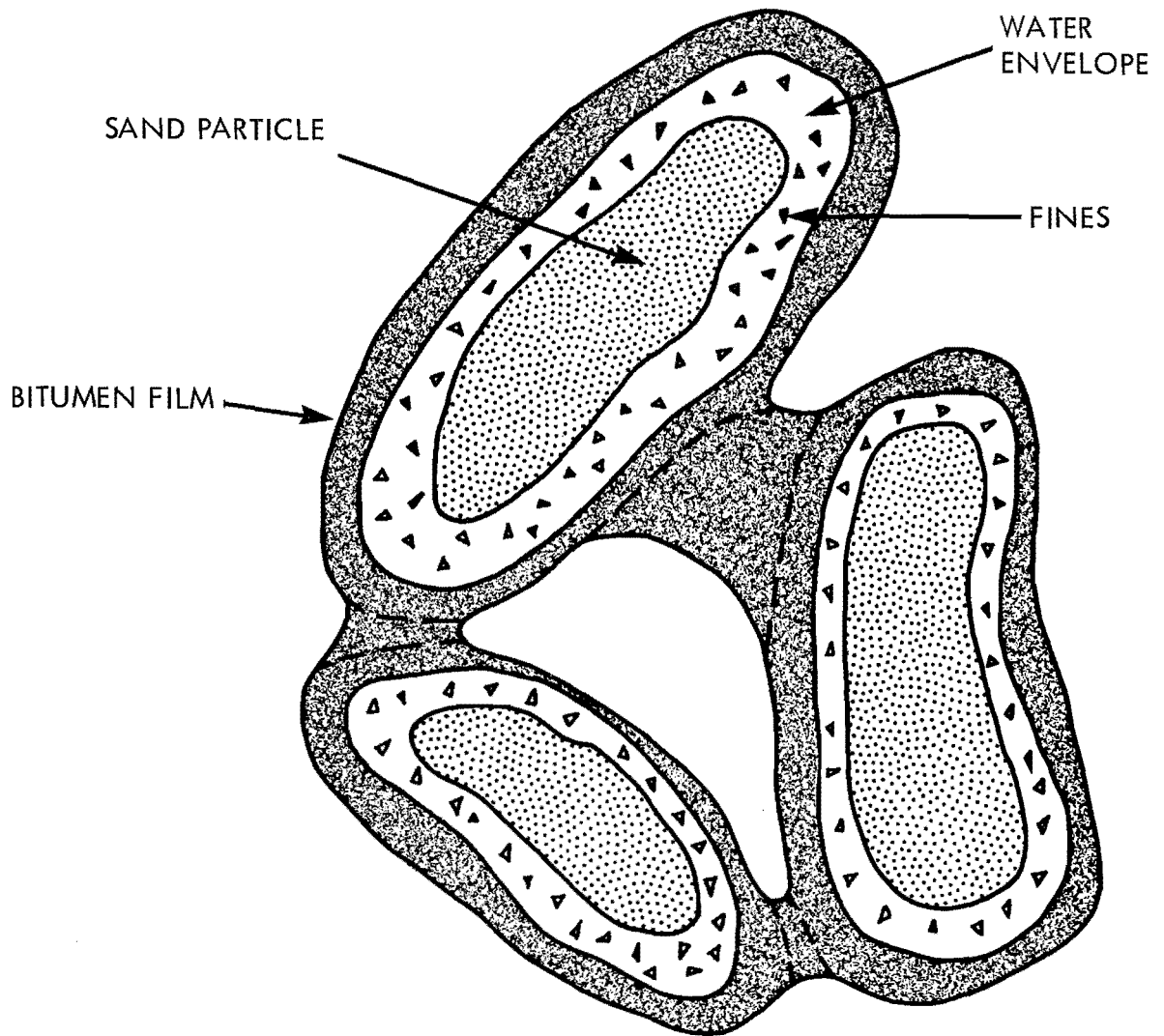
removed after freezeup. The system used to remove muskeg by Great Canadian Oil Sands employs 15-cubic yard front-end loaders and 150-ton trucks. The muskeg piles cannot be left unrestrained, since on melting the material spreads over the countryside, producing a very undesirable condition over a large area. In order to produce a reasonably orderly array of muskeg waste piles, a retaining structure of soil is built around them and the height of the muskeg dumps is restricted to 100 feet.

Eighty percent of the overburden is needed to build high dams around the pit to contain the future tailings. These structures can be 300 feet high and are built with surface slopes of 1 to 2.5 percent with impervious clay cores. The compaction of material controls the rate at which the structure can be built, and the main dyke construction can only be done when the materials are not frozen.

The average thickness of the ore body is 150 feet, and most of the oil sand is mined by two bucket wheels, each operating on a separate bench, one above the other. Transfer of the materials from the face to the extraction plant is accomplished by an articulated conveyor system. Some isolated pockets of oil sand occur which are not readily accessible to mining by the large bucket wheels; these areas are mined by the use of a small bucket wheel discharging into trucks which unload onto the trunk conveyor.

The extraction plant has four parallel independent processing lines. The fundamental steps in extraction are feed conditioning, separation of the bitumen, waste disposal, and cleaning the bitumen concentrate (Fig. 2).

Conditioning is achieved by mixing feed with water and caustic soda at 180°F to bring the pH to within 8.0 to 8.5 (without the addition of an alkaline agent the pH is 5.5 to 7.5). Each conditioning drum is a rotating horizontal vessel, 17 feet in diameter and 51 feet long. Oil sand, hot water, and dilute caustic soda for pH adjustment are introduced into the feed end of the drum, and steam is sparged into the drum under the surface of the pulp to maintain the outlet temperature at 180-190°F. The conditioned pulp at this point contains approximately 70 percent solids and is discharged from the drum through a screen to a feed sump. Any necessary make-up process water is added on the screen. Middlings recycle is added to the feed sump to maintain the proper density for pumping the slurry to the separation cells.



TYPICAL ARRANGEMENT OF TAR SAND PARTICLES (SCHEMATIC)

FIGURE 1

PRIMARY EXTRACTION PROCESS FLOW SHEET

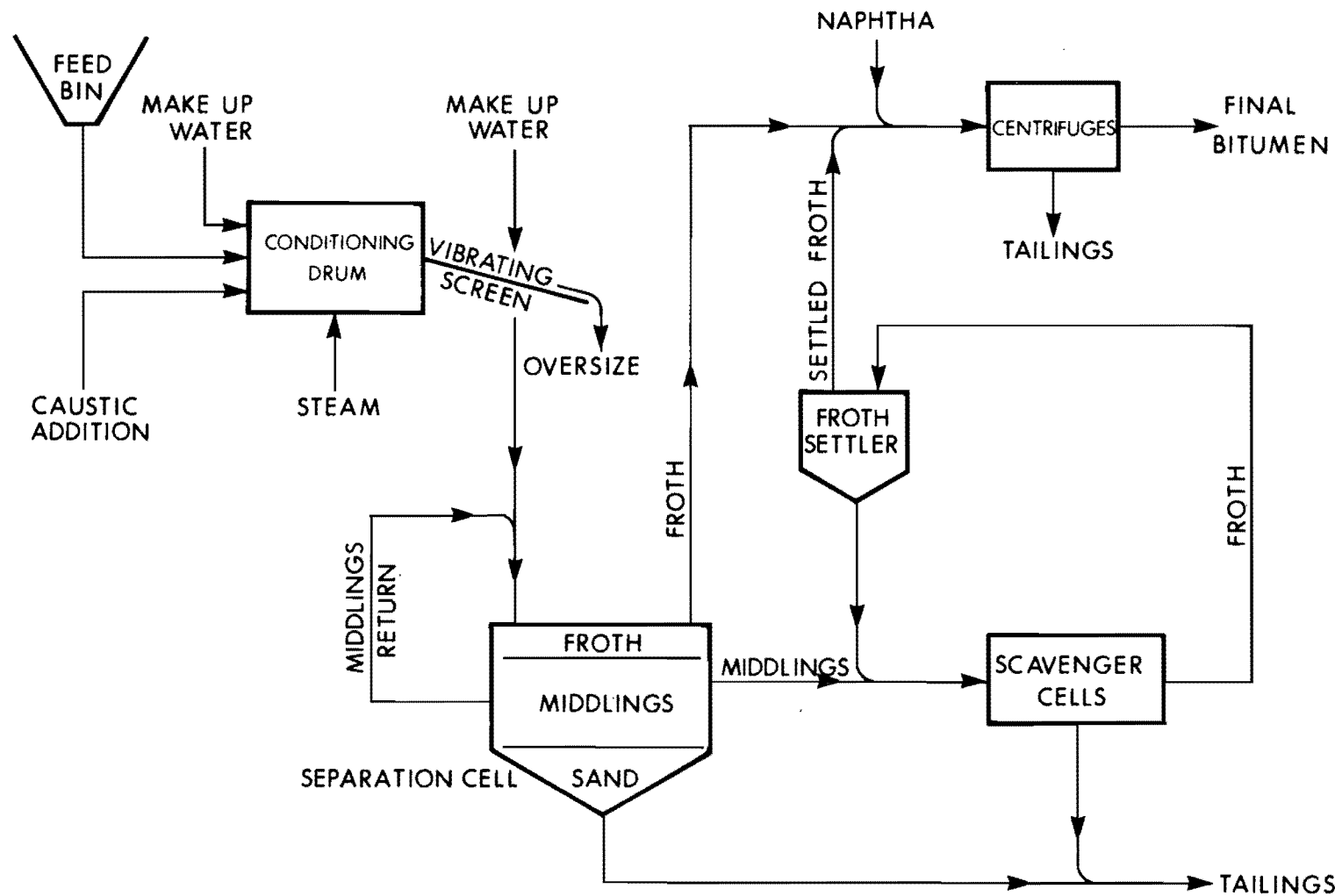


FIGURE 2

The separation cells are vertical cone-bottom vessels, 44 feet in diameter and 24 feet high, with a center feed well into which the diluted pulp is pumped. The froth which floats is skimmed by rakes to a peripheral launder where it is collected and pumped to the solvent extraction plant. The coarse mineral matter, which settles to the cone bottom, is raked to the center discharge and, thence, to a pump sump, where it is repulped with scavenger tailings and dilution water and pumped to the tailings pump house. These combined tailings are then pumped to the tailings pond.

The middlings stream is withdrawn from the side of the separation cell and pumped both to the feed sump for recycle and also to the scavenger circuit. The scavenger circuit consists of two banks of separator cells, each bank serving two processing lines. The cells are the largest conventional air-flotation units commercially available. The combined bitumen froth from all the scavenger cells, rich in water and mineral, is allowed to settle in the froth settlers; again, there is one settler for each two processing lines. The settler bottoms are recycled to the scavenger cell feed while the froth is combined with that from the separation cells as feed to the solvent extraction plant. The mineral product from the scavenger flotation cells is combined with the separation cell minerals as mentioned above. In the final extraction process, the combined froths arriving from the primary extraction at a temperature of about 160°F are heated with steam and diluted with sufficient coker naphtha to reduce the viscosity of the bitumen for centrifugation. The centrifuge process is conventional, using standard commercially available machines in parallel. The diluted bitumen product contains approximately 5 percent (by weight) water and 1 percent (by weight) mineral. The plant is designed for a recovery of 97 percent of the bitumen in the feed. The solid material removed by the centrifuges is repulped with water and pumped to the tailings pond. The diluent and water are removed from the bitumen by distillation and the diluent is recycled.

The tailings stream, about 24,000 gallons per minute, is delivered to the pond by pumps and has a clay to water ratio of about .075. In the tailings area the coarse fraction of the tailings, sand, is used to build the retaining dyke, while the slimes portion flows into the center of the pond where it settles to an initial clay to water ratio of about 0.14. Some of the

excess water in the tailings pond can be recycled as a substitute for fresh water. Some of the fines in the original oil sands are 2 microns and smaller in size and take a long time to settle; thus, recycle water contains a fair amount of "clay-size" material. When the tailings pond water is recycled, this material builds up and contributes to an increase in middlings viscosity. In general, recycle water having 10 percent or more of less than 2 micron size material is not suitable for recycling; but water having 5 percent of less than 2 micron size material can be substituted on the basis of 2 gallons of recycle water for 1 gallon of fresh water.

According to Allen and Sandford (1974), research studies are in progress to define the chemical, physical, mineralogical, and microbiological properties of tailings deposits. Concurrently, field studies to determine how tailings can be treated to improve their quality by the addition of topsoil, use of synthetic fibres, muskeg, and manure are also in progress, as are field revegetation experiments and "high-speed" laboratory growth experiments.

The fact that most of the lease is mineable, that the overburden swell factor is 7 percent, and the effective swell factor of tailings is 35 percent means that when the lease has been worked out the "land surface" to be reclaimed will be over 100 feet higher than the original surface. This factor will have to be taken into account in final reclamation plans.

Composition

The mineralogical composition of the clay-size ($<2\mu$) fraction of hot water process tailings is described by Camp (1976). This composition can vary over a wide range, according to the type and location of sand extracted, but in general major clay components are kaolinite (22-76%), illite (7-10%) and montmorillonite (1-8%). The presence of montmorillonite, a three-layer clay with pronounced swelling capability in contact with water, must be considered a significant factor in determining the dewaterability of tailings sludges. This is substantiated by the fact that qualitative data indicate that the better compaction currently being observed with tailings sludges at the GCOS facility is consistent with a lower montmorillonite/kaolinite ratio than in previous years. Illite, another three layer clay, differs from montmorillonite mainly in that potassium constitutes the predominant interlayer cation, and by virtue of favorable interactive forces this placement of potassium ion results in very much reduced swelling capacity. Although there is evidence that addition of excess potassium ion to montmorillonite suspensions can result in some decrease in its swelling capacity (p. 64, Kendall, 1974), this usually occurs only after repeated drying and wetting, and does not necessarily indicate conversion to an illite form (van Olphen, 1963). The possibility of the reverse conversion, that is, illite to montmorillonite, has fundamental ramifications in the production of clay slimes, and does not appear to have been fully investigated. A discussion of clay structures and properties is included in the Appendix.

Other minerals of less than 2μ particle size which are found in the tailings constitute chlorite, quartz, feldspar, calcite dolomite, siderite and ankerite, as well as zircon, illmenite, leucoxene and rutile, whose commercial recovery is discussed below.

The clay fraction of the tailings contains residual bitumen as well as dissolved organic materials. The former is the subject of further recovery efforts, also described below, and interaction of part of the latter with the particulate material is believed by some to increase the stability of the clay suspensions. Baptista and Bowman (1969) describe a study in which they found that certain components of the organic fraction of Athabasca Oil Sand were active in the flotation of solids, which can occur during the hot water

extraction process. They present evidence that water-soluble naphthenic salts act as frothers, and that carboxylic type organic complexes, adsorbed on the surface of the solids, act as collectors. Moschopedis et al (1976) report on the water-soluble constituents of Athabasca bitumen. The materials were extracted from Great Canadian Oil Sands tailings sludge, where it is suggested they stabilize the clay suspension and retard settling. The compounds were found to contain sulphonic acid, carboxylic acid and phenolic functional groups.

Gewers (1968) discusses the stabilization of bitumen-water emulsions by colloidal clays and asphaltenes. The discussion is directed toward understanding problems encountered in emulsion breaking during the recovery of bitumen and heavy oil from unconsolidated sand formations, and provides further insight into the interfacial characteristics of tar sands components.

Insomuch as effluent from the tailings pond area must reflect on the composition of the contained material to some degree, reports of analyses of tailings pond dyke filter samples are included in this section. A Scientific Enquiry Committee was appointed in 1976 by the Alberta Minister of Environment to investigate factors associated with the discharge of effluents from the GCOS tailings pond dyke to the Athabasca River. It was pointed out that the procedure followed in the GCOS dyke construction generates effluent which is absent in the more usual rolled earth fill placement procedure, and also results in a more porous structure requiring careful seepage control through a drainage system, to ensure stability. In November 1974 approximately 425,000 gpd were being collected by the drains and discharged to the river. At the time, information on the water quality characteristics of the dyke discharges was very limited.

Kupchanko (1968) had carried out preliminary studies on the compatibility of GCOS tailings pond water with the Athabasca River. This followed a request by GCOS for permission to discharge 110×10^6 ft³ of effluent from the pond into the Athabasca during periods of high flow. Specific recommendations were made as to rate of discharge. GCOS had monitored pH, oil, phenol and suspended solids in the period 1970-1974. Alberta Environment carried out comprehensive analyses on three samples collected on separate dates in November 1973 and five samples collected in June 1976. Hrudy (1975) reported on the characterization of wastewaters from the Great Canadian Oil

Sands bitumen extraction and upgrading plant. The dyke filter drainage from the tailings pond was found to have a high organic carbon content, and to be acutely toxic to rainbow trout with an $LC_{50} < 20\%$. A repeat sample of the drainage was analyzed at the Environmental Sciences Centre, University of Calgary, and four specific compounds, butylated hydroxytoluene, di-n-butyl phthallate, bis (2-ethylhexyl) phthallate and bis (2-ethylhexyl) adipate, were identified by GC-MS. Tailings pond dyke filter drainage samples collected in 1975 have been found to contain 100-120 mg/l of total organic carbon, 69% of which was extractable with organic solvents (Stroscher and Peake, 1976).

Ninety-two percent of the extractable carbon was in the form of oxygenated compounds, including organic acids (79%), phenols (4.5%), ketones (2.7%), aldehydes (1.9%), organic acid esters (1.5%), amides (1.0%), and quinones (0.2%). Organic sulfur compounds averaged 5.3%, organic nitrogen compounds 1.1%, and hydrocarbons 0.04% of the extractable material. Iron (0.25 mg/l) was found to be the most abundant metal in drainage samples, followed by manganese (0.02 mg/l). Vanadium was also present in low concentration (0.001-0.002 mg/l). Diffusion studies in the Athabasca River have also been carried out to estimate dilution factors and are detailed in the report of the 1976 Scientific Enquiry.

Microbial Population

The significance of the role of microorganisms is not usually considered in general discussions on clay tailings ponds. This is due mainly to the fact that in most cases where inorganic materials such as bauxite, specific clays, and phosphates are being mined, the tailings ponds created do not, at least initially, contain concentrations of organic components which could support significant heterotrophic bacterial populations. In these ponds only low levels of slowly metabolizing bacteria are encountered with occasional blooms of specific autotrophic organisms which utilize CO_2 or carbonates as sources of carbon and derive energy from certain inorganic oxidation reactions. Ultimately a carbon cycle will be established and increased microbial activity will appear. This process often takes decades to be set into motion.

Tailings emanating from a tar sands extraction plant present a different picture. From the time they are created, these tailings contain a host of organic materials of varying complexity. These compounds result from the reaction of hot, alkaline waters with the bitumen of the tar sands material. The GLC profiles of extracted materials from the G.C.O.S. tailings waters presented in the report by Strosher and Peake (1976), as well as earlier work by Kupchanko (1968), Duncan (1972), and Moschopedis *et al.* (1976), confirm the presence of many organic components. These materials must be considered as potential food and energy sources to microorganisms in these tailings waters. Thus it is not impossible to envisage some microbial activity within a tar sands tailings pond soon after production begins.

A further factor that could be potentially stimulatory to microbial activity, at least at the present time, is the high pond temperature that remains in the 60°F region during the entire year. Such a temperature, especially in winter, could mean that metabolism is not dependent on season. Hence ultimate microbial development might well occur more rapidly than initially anticipated.

There are also certain complications which could potentially retard microbial development. Firstly, the organic components present in the pond are, for the most part, derived from bitumen. Although a great many of these components are not yet identified, it is known that most are heterocyclic, aromatic, and/or branched in nature. This almost certainly implies an intrinsic recalcitrance to microbial attack. Thus the bacterial population existing in the present G.C.O.S.

tailings pond does not have access to a readily available carbon source, although it is known that populations can develop which are capable of utilizing certain portions of these components. The second complication concerns inorganic nutrition of the microbial population. Because of the nature of the tar sands deposits, tailings derived from these materials are certainly deficient in utilizable nitrogen and probably phosphorus. This, in the long run, may not prevent growth of bacteria but is certain to influence the overall rate of development. It is a classic fact, that bacteria are exceedingly efficient in scavenging those nitrogen and phosphorus resources that are available and recycling them during growth. Thus sustained microbial development is still a real possibility. A third complication concerns the nature of the bitumen extraction process itself. It is known that native oilsand material contains a detectable microbial population throughout its depth (Jobson et. al., 1974), and the hot and alkaline extractions of the bitumen which would be expected to destroy the majority of viable organisms may not eliminate spore-forming bacteria such as Bacillus sp., Clostridium sp., and Desulfotomaculum sp. Additionally, upon delivery into the tailings pond, inoculation of viable organisms from airborne dust particles will certainly aid in re-establishing a more generalized microbial population. Results of a study by Cook (1976) on samples of drainage water are tabulated below:

<u>Location</u>	<u>Bacterial Count/ml of Drainage Water</u>
Water from standpipe	3.0×10^6
Boat launch site	1.9×10^6
Sump	3.6×10^6

The level of these counts, as well as the fact that approximately 20% of the counted colonies were Cytophage sp., indicates the discharge has a bacterial load similar to average fresh water. Cultures of Clostridia and Desulfovibrio were also enriched from all three samples. Since the above levels of microorganisms are detectable in the discharge, it is probable that similar, if not increased counts are present at certain levels within the pond itself.

Not only is it certain that some kind of microbial development is occurring in the present G.C.O.S. tailings pond, but it is probable that this population is stratified into at least three regions. The upper layer is composed

of less than 5% solids topped with a floating mass of residual bitumen material. It is supposed, but not yet proven because of the lack of appropriate studies, that this uppermost region will be, or is, the site of significant microbial activity. This activity, if it exists, will likely be at the expense of bitumen components floating at the surface. The degradation products and cellular debris from this surface activity may well provide growth substrates for microbial populations present at greater depths within the pond. The relatively clean intermediate depth waters of the present tailings pond will likely contain a bacterial population dependent upon water-soluble bitumen components as a source of carbon and energy. To what extent this is occurring is not yet known, and awaits studies to substantiate the hypothesis. The lower "sludge" layer, containing 5-30% solids, will primarily be an anaerobic region where considerable microbial development may occur. Again, this is supposition, and is not yet proven by hard experimental data. As well, it is not yet clear which of the three regions in the pond will develop microbial populations most quickly and whether any of these populations will have a detrimental effect on the surrounding environment. Such effects could take the form of gradual acidification of the pond waters, production of unpleasant and odoriferous compounds, or possible carcinogenic metabolic products which could gain access to the watersheds within the region. These possibilities cannot, at present, be confirmed or refuted since the existing G.C.O.S. tailings pond has not even been characterized as to its overall microbial composition. It is also far from clear whether or not any manipulation of the pond, such as aeration or addition of sewage effluent would have a beneficial or damaging influence to the overall pond environment. Certain researchers believe that any process which leads to microbial proliferation within the pond would be beneficial. They feel that such microbial activity would aid in the flocculation and consolidation of the clay "slime" layer within the pond and would yield more recyclable alkaline water to be used again in bitumen extraction. Indeed, Raymond *et. al.* (1970) in their patent (see p. 26) claim that incorporation of viable bacteria into pondwater enhances its settlability. They specify Micrococcus, Corynebacteria, Nocardia, Pseudomonas, Mycobacterium, Streptomyces, Aspergillus (actually a fungus), Acetobacter, and Achromobacter as candidate organisms. Although no

evidence is presented for the specific utilization of these genera, the method is based upon bacterial growth within the clay tailings, which growth, it is also claimed, can be stimulated by the addition of nutrients. It may be that attached extra-cellular polysaccharides produced by such microorganisms can accumulate and retain clay particles and thus carry them out of suspension. The effect of the dead bacterial cells on the dewaterability of the sludge may also be beneficial. Jobson (1976) has found that addition of sterilized ammonium chloride to standing columns of tailings sludge resulted in significant hydrogen sulfide generation as compared to unamended controls. It should be noted that although this specific treatment only produced obnoxious odours and did not cause significant settling of the clays, addition of aliquots of certain pre-grown microorganisms to other columns of tailings ponds materials did enhance settling over control columns. Again, black ferrous sulfide accumulations were observed.

At the present time it is unclear what level of microbial activity exists in the G.C.O.S. tailings pond. Additionally, it is not known whether it would be beneficial to stimulate the population, if, in fact, any such stimulation is economically feasible, or whether microbial growth in such ponds should be suppressed in the long run. Only through sustained microbiological investigations in G.C.O.S. and subsequent tailings ponds will answers to some of these questions be found.

Flocculation and Sedimentation

The large area of the GCOS tailings pond (about 1 sq. mile) enables the clay tailings to sediment sufficiently to provide water for recycle to the extraction operation. A detailed description of the GCOS pond is included in the article by Camp (1976). Designs for the Syncrude plant incorporate a pond of even larger area, and Syncrude will have approximately double the tailings volume of the GCOS plant to contend with. An initial tailings area of nine square miles is planned on the plateau near the plant and mine area for disposal during the first six years (Oilweek May 6, 1974). The company has contended (Can. Petrol., Nov. 1973; Syncrude, 1973) that there would be no accumulation of water after the first three years of operation, since about half the water used in the plant would be recycled from the tailings pond and that evaporation and percolation would also help maintain the balance.

Several patents and reports appear in the literature which address increasing the efficiency and rate of the sedimentation process by the addition of flocculants or various other procedures. Baillie (1968) describes a method in which effluent discharged from the extraction plant is discharged to an upper portion of a sand pile zone which slopes downward to the tailings ponds. He claims that some of the mineral fines contained in the effluent are filtered out by this process, and that evaporation, as a result of the increased exposure while the effluent filters through the pile, reduces the final effluent volume. Baillie (1969) has also patented the use of flocculation followed by centrifugation for the treatment of the clay-containing waste streams from the hot water process. The patent lists a range of chemicals, as well as the use of pH adjustment, as effective in causing flocculation to occur. Hepp and Camp (1970) also have patented the use of flocculation followed by vacuum precoat filtration for the treatment of hot water process discharge water. Libor (1972) has patented the application of various flocculating agents for the concentration of the solid content of aqueous solutions containing clay minerals. Schulz and Morrison (1973) have examined the flocculating ability of a number of commercially available flocculating agents in the treatment of tailings pondwater. Stastny (1973, 1974) has found that injection of carbon dioxide into

samples from the GCOS tailings stream aids flocculation and settling. The results from this study do not preclude the possibility that the effect derives from the consequent lowering of pH, since Baillie (1969) and Schutte (1974) describe pH reduction itself as causing flocculation.

Lang (1973) has patented various polymers and graft copolymers for flocculating oil- and clay-containing slimes. The use of various water soluble polymers and copolymers based on acrylic acid is described. The polymers are claimed to be particularly useful in flocculating suspensions of finely divided clay and silica particles in intimate association with hydrocarbons, and the use of secondary flocculants is discussed. Specken (1975) evaluated a range of coagulants and flocculants, known to be effective in clarifying drilling site sump waters, for use in the clarification of wastewater derived from tar sands processing. Nineteen commercially available polyelectrolytes were tested, either in a one step process or following aeration or treatment with permanganate. Aeration was found to have no significant effect, whereas permanganate addition, followed by polyelectrolyte, appeared to be most effective. It is possible that the permanganate may derive its effect from conversion to manganese dioxide, which would be deposited on the clay particles, as in the production of greensand. Specken also found that simultaneous sedimentation of flocculated clay and sand, or more probably sequential sedimentation of flocculated clay and sand, should produce a final sludge with a higher clay/water ratio than that produced by settling flocculated or non-flocculated clay alone. Chemical costs for a combined permanganate/polyelectrolyte flocculation sequence are estimated at 11¢ per barrel bitumen produced.

Schutte (1974) describes the flocculation of clays and other small solids particles present in the middlings and tailings streams by the reduction of pH within the range 5.5 - 6.5 by the addition of $2.0 - 5.7 \times 10^{-4}$ b sulfuric acid per g of solid material. He further claims that if the clarified water is allowed to remain in contact with the settled sludge for from 1 to 7 days the pH recovers to 7.0. It is possible that chemical changes within the clays themselves provide such buffering action.

Camp (1970) has patented a process in which fines are concentrated in the interfacial region between the aqueous tailings phase and an

immiscible organic layer, such as kerosene, with subsequent withdrawal and treatment of the interfacial region. Surfactants may be added to increase the efficiency of the process.

Raymond et al (1970) have patented bacterial treatment of hot water process effluent discharge. They claim that the settling of the clay is facilitated by incorporating viable microorganisms into the water, which remove hydrocarbons by sorption and cause change in the settling properties of the effluent. Whether the sorption precedes metabolism or not is unclear.

A process for clarifying tailings pondwater by the application of high intensity sound waves is claimed by Fear and Camp (1972). The sound waves are described as setting up elastic wave action in the pondwater, resulting in the separate agglomeration of clay and bitumen particles. The sound wave treatment could be supplemented by the prior addition of flocculating agents.

Maloney (1976) has been issued a patent in which tailings pond water is clarified by agglomeration with unextracted tar sands.

The clarification of silica and bentonite suspensions and diluted sludge from the GCOS tailings ponds using electrophoretically assisted gravitational sedimentation was investigated by Flintoff and Plitt (1976). Results indicated that good clarification could be achieved with silica, but that only limited clarification could be achieved with the bentonite and tar sands tailings. The method was considered economically unattractive for the treatment of bentonite and tar sands tailings.

Sludge Dewatering and Disposal

Final disposal of tailings in an environmentally acceptable form represents a last stage in a mining venture. It is part of the abandonment procedure. If a large part of the clay hot water process tailings sludges could be dewatered beyond their present solids level before this is carried out, this would ensure stability and decrease the hazards associated with a worked-out area. Various schemes that would result in higher solids-content sludge have been investigated.

Freeze-thaw dewatering of sludge resulting from agglomeration or flocculation of pondwater or any other clay suspension has been described by Elliott (1975: see also p. 52). The solids content of the sludge can be raised from typically less than 10% to around 30% by weight using this procedure. The process was not found to work well with un-flocculated suspensions, and the amount of solids compaction increased with the number of freeze-thaw cycles performed.

A process in which a mined-out cavity is used in the solids separation train was patented by Schutte (1975). In this process the stream, comprising water and coarse and fine solids, is first fed into the mined-out cavity to settle the coarse solids. Some of the decanted water is transferred to a large settling pond for clarification, with the remainder being returned to the plant and added to the tailings stream to fluidize it and render it pumpable. It is claimed that advantages are derived from the process in that some of the fines are trapped in the sand in the cavity, reducing the volume of sludge generated in the settling pond, and that the use of decanted water to fluidize the tailings reduces the overall water consumption of the extraction process.

Ashton and Davitt (1976) claim a method for storing sludge in a manner that does not negatively affect the local environment and that provides a means for the recovery of additional bitumen from the sludge. The sludge is transferred to a receiving zone consisting of a well or tank which communicate with a generally larger open storage area containing a surface layer of substantially unpolluted water. The communication channels are subsurface, and hence the bitumen released in the transfer rises to the surface only within the confines of the receiving well. Redispersal of the sludge layer by climatic

conditions is minimized by the addition of a flocculating agent to the unpolluted portion of the storage pond.

A method has been patented (Baillie and Fear, 1976) in which the waste water stream from the extraction plant, containing sand, silt, clay and bitumen, is dispersed over the surface of the tailings pond. This is said to "rain" the sand fraction into the sludge layer, compacting it and eventually storing it within the interstices of the packed sand (see p. 52).

Bakhshi (1975) investigated the treatment of oil sands tailings with fly ash and subsequent filtration of the mixture (see p. 52). A fly ash dosage of 6 g/50 g tailings gave the best results, with a fairly dry filter cake and 59% water recovery. However, if the treatment were to be utilized on a full scale level, daily fly ash requirements would be about 2140 long tons based on 1975 GCOS production data.

Baillie and Fear (1976) suggest using settled sludge from the tailings pond as a carrier to aid in the conveyance of the sand tailings layer to the retention pond. This is similar to the concept of repulping sand tailings with sludge prior to conveyance, in the phosphate mining industry in Florida (see p. 53, Bromwell, 1977).

Water may be removed and cementing agents may be produced in clays by electrical methods. When an electric gradient is applied to a charged capillary between two electrodes, water moves toward the negative electrode. This phenomenon is known as electroosmosis and has been used to dewater clay minerals. Electrochemical changes also occur in the clay and result in cementing and irreversible hardening (Morley and Parry, 1971). Significant hardening has been found to occur in montmorillonites by the precipitation of hydroxides in the interlayer positions converting the montmorillonites to a chlorite-like clay (Gray, 1970). Several engineering design approaches have been formulated (Gray, 1967; Bjerrum, 1967) but do not appear to have been put into practice.

Hepler (1977) and co-workers are currently investigating the coagulation and settling of clay in water and in aqueous systems containing combinations of bitumen and substances derived from bitumen. They are also investigating some physical and chemical properties of clay sludges that contain from about 20% to about 50% clay, with most of the balance being water.

Materials Recovery From Tailings

Materials recovery from the hot water process tailings could result in reduction of the final volume requiring disposal. Even if this reduction were not significant, the process of removing the recoverable material may result in the tailings becoming more environmentally acceptable and perhaps easier to stabilize. For instance, bitumen removal from the clay tailings may increase their eventual dewaterability, and will in any case remove a hazard to wild life and a barrier to any recreational use of a tailings disposal area. The economic benefits of materials recovery are obvious. Bitumen recovery while en route may more than cover the cost of pumping clay sludges to final disposal areas.

Baillie (1970) has patented the process of removing bitumen scum, which rises to the surface of settling ponds, with wiper blades. Although the bitumen has a higher specific gravity (1.05 - 1.10) than the pond water (1.00 - 1.03) it is believed that it floats due to attached air.

Davitt (1975a, b) has patented the use of hydrocyclones in improving bitumen recovery from settling cell tailings in the hot water process, and in bitumen recovery from other process streams (1975c,d). He has also been issued a series of patents concerning the recovery of bitumen from the lower, or sludge, layers of the tailings pond. One method involves transfer to a settling zone area at any temperature in the range 40-200°F, and allowing the bitumen to separate as an upper froth layer. Improved bitumen recovery, especially at high temperatures, can be accomplished by the addition of sodium silicate (1975e). The other methods are based essentially on dissolved air flotation (1975f) and dispersed air flotation (1975g,h,i), again with improved recovery on addition of sodium silicate.

Coke has been considered for removal of bitumen from the middlings and sand tailings layers from the primary extraction step (Hudson and Seitzer, 1971). Tollefson (1976) is currently investigating the use of coke to recover bitumen from GCOS plant 3 and plant 4 tailings. Interim reports indicate some degree of success, although coke requirements are stated as being large.

Goforth et al (1976) describe research in the upgrading of a crude hot

water process tailings stream to produce quality zircon and titanium mineral products, the latter including rutile, leucoxene and ilmenite fractions. They evaluate heavy minerals distribution in tar sand drilling core samples for various locations of Syncrude Lease 17, and estimate annual production levels for the heavy minerals when the Syncrude plant becomes operational. A preliminary economic evaluation of the potential for zircon, ilmenite-leucoxene and rutile production is included in their report, as well as consideration of the economics of upgrading the ilmenite and leucoxene to synthetic rutile suitable for pigment use. Kramers and Brown (1975) have evaluated samples from test wells distributed throughout the surface mineable area of the Athabasca Oil Sands to determine the amount of heavy minerals present, and in particular the titanium and zirconium contents. They conclude that on the basis of preliminary calculations, the tailings stream from one oil sands plant would provide sufficient feed for a large scale titanium dioxide pigment plant, and sufficient zircon feed to satisfy Canadian demand for metallic zirconium. They point out, however, that heavy mineral potential should be evaluated in detail for each mine site.

Hartman (1966) has described an attempt to produce glass grade sand from tar sand tailings, using iron determinations to follow the degree of beneficiation. Clark (1973) reviews processes such as flotation, differential precipitation, two-liquid separation and magnetic separation in the recovery of materials from clay slimes.

Reduction by Process Modification

It may be possible to limit sludge accumulation by process modification, provided bitumen recovery is not significantly reduced. A fairly effective method described as selective mining (Camp, 1976), has been employed in this respect by GCOS. Lenses of clay or fines are rejected during mining, substantially reducing process clay input.

Various procedures have been investigated for increasing bitumen recovery in the extraction process without a penalty in an increase in water requirement. It is possible that similar procedures could be used for decreasing the overall water usage. In an improved version of the hot-water extraction process patented by Cymbalisty (1974) the primary extraction step is carried out in two vessels, the first one consisting of a sand separation cell, and the second a flotation cell. Because the sand is removed before the froth separation of the bitumen, improved froth quality and recovery are realized. The fines from the froth separation cell are then recycled to the vicinity of the tailings outlet from the sand separation cell, eliminating them from the system without the need for a middlings dragstream. It has also been proposed (Davitt, 1975a) that hydrocyclones be used in the initial removal of sand and coarse material prior to the froth separation step. Cymbalisty (1975) also discusses dilution of the middlings stream with hot water to facilitate flotation of residual bitumen, with return of the tailings stream from this step to the front end of the extraction process.

Current operating procedure maintains the ratio of clay to water in the separation cell middlings below about 0.12. Above this level, the viscosity of the middlings rises above 5.7 centipoise and primary froth yields in the separation cell decrease drastically.

Camp (1971) has patented the use of ion exchange resins in removing divalent and trivalent ions from clay-containing water fractions in the hot water extraction process. This removal makes possible increased recycle of these streams into the process, since it was found that an operable middling viscosity could be maintained in the primary separation cells at clay/water ratios greater than 0.1 in the absence of these ions. The clay-containing water fractions selected for treatment with the ion exchange process are the middlings

stream and pondwater containing suspended material.

Camp (1973) has also patented the use of clay deflocculants, such as condensed sodium silicates and phosphates, and sodium lignosulfonates, in making possible high bitumen froth recoveries at clay to water ratios above 0.12. This procedure would reduce water requirements in the primary extraction step.

TAILINGS FROM OIL SANDS EXTRACTION PROCEDURES OTHER THAN THE HOT WATER PROCESS

General Comments

Flock (1975) provides a good review of possible methods of recovery of bitumen from the sands, apart from in situ methods already in the pilot plant stage. For instance, he considers heating by electrical energy, whether by an electrovolatilization, electrothermal or electromagnetic mechanism, uneconomical due to the inherent inefficiencies of electric power production. The feasibility of the use of bacteria and enzymatic chemicals is also considered to be uncertain. He suggests that the most promising unconventional in situ method would involve the use of nuclear devices. He addresses the possibility of subsurface mining of oil sands and reviews unconventional extraction procedures for mined sand, such as cold-water separation, sand reduction, solvent extraction and direct coking.

Many of the methods considered in this section have not progressed even to the pilot plant stage, and comments on the production of tailings and waste streams in these instances must be considered entirely speculative.

Sand Reduction Methods

The category of sand reduction methods has come to include those in which the sand is separated from the bitumen by milling, kneading or agitation in the presence of hydrophilic or hydrophobic surfaces. Puddington (1968) has patented such a system, in which a hydrophobic phase is recovered as agglomerates when agitated in the presence of hydrophilic surfaces, or as an adherent layer when agitated in the presence of hydrophobic surfaces. Direct application to bitumen recovery from oil sands is demonstrated in each case, after addition of water and under various conditions of temperature and pH. The use of oleophilic roll surfaces and oleophilic moving belt surfaces for fluid hydrophobic material recovery and of fluid oleophilic layers for solid hydrophobic material recovery is also claimed. Puddington (1971) later describes the adaption of oil phase agglomeration to continuous operation for the separation of bitumen from oil sands, and has also patented a plant design in this regard (1976). A major advantage of the method is cited as the ability to handle oil sands with high fines contents. Although this type of separation procedure would be expected to produce a liquid tailings stream, the solids content would likely be very much higher than in the hot-water extraction process, possibly allowing direct disposal into mined-out areas.

According to the 1976 Progress Report of the Division of Chemistry, National Research Council, the spherical agglomeration method is now also being investigated in the reverse configuration, where the oil sands is mixed with a suitable bitumen solvent, and sufficient water added to enable the mineral content, including sand and clay, to be removed as the agglomerated material. The tailings stream from this extractive procedure would thus be semi-solid and even more acceptable for disposal, possibly even in an unrestrained form.

Kruyer (1976) is investigating a method of separating bitumen from oil sands also based on the former's affinity for oleophilic surfaces. The method in its simplest form consists of placing a slurry of oil and water on an oleophilic screen immersed in water. The screen is agitated to allow sand passage while the bitumen is attracted to the oleophilic surface of the screen. Slurry is added to the screen until the accumulation of bitumen on the screen hinders the passage of the sand. The screen is then removed from the water and bitumen recovered from it.

A small pre-pilot plant scale version of this method, using a perforated rotating drum as the separating screen, has been constructed, yielding a bitumen product containing in some cases less than 15 percent solids, and a sand product containing less than 0.4 percent bitumen. In these tests, about 98 percent of the bitumen present in the oil sand feed was recovered in the bitumen product. The perforated drum was 12 inches long and 18 inches in diameter, and gave an oil sand throughput of 100 pounds per hour. The tailings stream from this process contained both sand and clay fractions, with the bulk of the clay being contained in the interstitial water between the sand grains. Some fines remained with the bitumen. Their quantity and methods for their removal are yet to be fully characterized. Addition of caustic soda in the process is not required, and the tailings are altered from their initial state only in that they have been separated from the bitumen. This should be advantageous in respect to reclamation.

Cold Water and Solvent Extraction Processes

The cold water process consists of grinding and disintegrating a mixture of bituminous sand, diluent, soda ash, wetting agent and some water in a low-discharge pebble mill (Djingheuzian, 1951). The slurry is further diluted in more water and separated in an agitator, followed by a rake classifier, where the bitumen-diluent oil is floated in the water and the sand sinks by gravity separation; the oil slurry is further settled in two-stage thickeners. The rate of production of tailings for this process was calculated to be of the same order as for the hot water process.

In contrast, solvent extraction is based on the presumed characteristic of the silica sand grains to be wetted by a very thin water envelope, which also contains fines (p. 13, Camp, 1976). The successful process dissolves the bitumen without breaking the water-fines envelope; it must thus maintain a sufficiently large interfacial tension between the bitumen-solvent and the connate water. As developed by Cottrell and Leary of Cities Service Athabasca Inc. during 1959-1961, it is a counter-current solvent extraction with steam stripping to recover solvent from the tailings. A high solids content tailing, possibly suitable for immediate backfill, should be realized from such a process.

Although sustained research efforts in these areas ceased when the hot water process was selected for commercial development, such methods, or combinations thereof, are proposed from time to time in the literature. For instance, counter-current solvent extraction of tar sands in an inclined rotary drum is described in a patent issued to Barr *et al* (1964). The solvent stream emerging from the drum may contain water and some fines, but nevertheless is claimed to be suitable for direct feed into a coker. The waste stream consists of water, sand and clay with residual bitumen and solvent, but presumably would be suitable for direct disposal into mined-out areas since the fluid content should be low. A variation of the cold water process has recently been developed by Fairbanks (Oilweek, 1975) specifically for exploitation of Kentucky oil sands deposits. It is claimed to be suitable also for oil sands from the Athabasca region, and might be considered to produce tailings somewhat similar to the above.

Baswick (1976) has patented a method for the ultrasonic separation of bitumen from tar sands using wave transmitting fluids such as methylene chloride. The environmental implications of the process are not discussed, but it is possible that severe restrictions would be placed on the disposal of tailings that contain residual chlorinated hydrocarbon solvent.

Direct Coking

Anhydrous extraction of hydrocarbons from oil sands by coking is discussed in a report by Moore et al (1975). Retorting processes depending on both indirect and direct heating are considered, and recommendations made for fundamental studies in the area. It is pointed out that such methods would produce a dry sand tailing, thus reducing the size of the sand reject area, and could be applied to tar sand deposits that are not water wet. Flynn (1975) reports on a study carried out at Syncrude on heat and mass balances for the direct coking of Athabasca Tar Sands, and concludes that this remains an attractive alternative to the hot water method for processing mined deposits.

A dry distillation method of recovering bitumen from mined Athabasca oil sands, which would eliminate tailings ponds associated with the hot water process and produce a thermally treated bitumen of lesser viscosity and lower density, has been proposed by Lurgi Canada Ltd. , and Lurgi Mineraloeltechnik GMBH of Frankfurt (Oilweek, Oct. 1975). Sand crackers, in which sands is used as a heat carrier, are central to the process.

Fine dusts can present a significant problem after the disposal of dry tailings, and it is possible that, in the event direct coking methods are operated on a commercial basis, special attention will have to be given to controlling their formation.

In Situ Recovery

Various agents can be injected into oil-bearing formations to facilitate the flow of oil through the formation (see for instance Boyle, 1959). It is likely that similar agents will be used in in situ recovery methods. Likely compounds comprise surfactants and dispersants, such as sulfonates and water soluble polymers, some of which will eventually emerge from the oil sands formation with the bitumen emulsion. It is probable that the major portion of these agents will remain with the bitumen fraction after separation and hence enter the upgrading plant. The environmental and process consequences of the portion remaining with the aqueous fraction are as yet unknown.

Although some pilot plant studies have been completed in the area of in situ recovery (see Redford, 1976), little discussion has been accorded to the possibility that solid particulate material may be produced with the emulsions, possibly carried in the interfacial regions. If produced in significant quantity this material would present a unique disposal problem, in that there would be no mined-out areas into which it could be backfilled.

Of potential importance are in situ methods based on the use of nuclear explosives for heavy oil recovery. Such a method was described in a proposal that was offered to industry by Phoenix Canada Oil Co. Ltd. (see Oilweek, 1974). The proposal visualized a 10 kiloton fission device releasing both thermal and shock energy to convert otherwise immobile viscous oil deposits into conventionally recoverable hydrocarbons. It was suggested that the resulting subterranean detonation cavern might also facilitate secondary and tertiary in situ recovery methods, such as steam injection and fireflood. Environmental implications of such a project are manifold. Convincing arguments, based on projects Gasbuggy (New Mexico, 1967), Rulison (Colorado, 1969) and Rio Blanco (Colorado, 1973), are presented which show radiation hazard from fission products to be insignificant. The formation of fission products has been minimized by the use of new so-called "clean" nuclear devices, and would be virtually eliminated in the event that a practical non-nuclear trigger is developed for the fusion reaction.

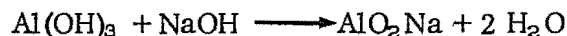
CLAY TAILINGS FROM OTHER EXTRACTIVE INDUSTRIES

Bauxite Mine Tailings

Bauxite is the principal ore of aluminum. It consists of aluminum oxide, more or less hydrated as $\text{AlO}(\text{OH})$ or $\text{Al}(\text{OH})_3$, and containing various impurities, such as iron oxide, kaolinite, titanium dioxide, quartz, and compounds of phosphorus and vanadium. Although it cannot thus be considered a pure mineralogical species, the term has come to be used for rocks of mineral deposits in which alumina preponderates. Deposits of bauxite are widespread (Kirk-Othmer Encyclopaedia of Chemical Technology, 1963), occurring in Europe, North and South America, U.S.S.R. and Africa. In Australia some very large deposits have recently been discovered in the north, on the west coast of the Cape York peninsula and on the Cove Peninsula, and in the south-west, around Perth.

All the alumina produced commercially in the world, with one or two exceptions only, is extracted from bauxite. Manufacture consists of separating the alumina from the various impurities of the bauxite, a process accomplished wholly by chemical means. For this purpose, advantage is taken of the amphoteric properties of the aluminum ion, which permit the metal to be solubilized in the form of sodium aluminate.

The most common process in this regard is the Bayer process. This is carried out entirely in the aqueous phase, by dissolving alumina hydrates in caustic soda solution, in accordance with one or the other of the following equations:



These solubilities depend on the caustic soda concentration and on the temperature. A closed circulation of caustic soda solution is employed, in which the following operations may be performed in turn:

- (1) Solution of the alumina, at a high temperature and by the use of a high caustic soda concentration;
- (2) separation of the insoluble impurities of bauxite and their

- washing in order to recover the caustic soda;
- (3) partial precipitation of the alumina trihydrate at a lower concentration of caustic soda and at a lower temperature;
- (4) regeneration of the solutions necessary for dissolving the alumina by evaporation of the water introduced for the washings;
- (5) finally, transformation of the trihydrate to anhydrous alumina by calcination at 1200°C.

The insoluble residues remaining after attack of the base are commonly known as red muds. They embody the iron oxides from the bauxite as well as some sodium alumino-silicate, which is an insoluble ternary compound produced by transformation during the attack upon the aluminum silicate (kaolinite) of the bauxite; some titanium oxide (TiO_2) and various other secondary impurities of bauxite are also present. The presence of well-defined swelling clays has not been recorded.

Generally the muds contain very fine particles ($<1\mu$) which are difficult to separate and wash. These operations are usually performed by continuous decanting and by the washing of successive solutions and decantations, counter-currently. The lyes from the washing, which have a low caustic soda concentration, are added to the lyes that were used for the attack; this dilution facilitates decanting of the muds, which is carried out at about 100°C, and also aids in the final precipitation of alumina. For the usual bauxites rich in Fe_2O_3 the quantity of muds to be washed is very large, amounting to 1000 kg or more for each 1000 kg of alumina, so that these operations call for very large facilities for continuous decanting or thickening. In exceptional cases, in the treatment of certain high-quality bauxites such as those from Guiana which furnish a small amount of mud, the separation and washing can be done by filtration.

Red mud tailings are usually stored in dyked-off disposal areas. Miners (1972) describes one such disposal area at the Arvida Works of the Aluminum Company of Canada Ltd. , The Bayer process for upgrading bauxite ore here results in the production of approximately 2/3 of a pound of "red mud" tailings for each pound of alumina produced. The tailings consist of 15 - 30% solids slurry comprising coarse bauxite and quartz particles with fine material described as a "ferruginous clay". Early clay dykes were prone to failure,

and were subsequently replaced by dykes constructed in the manner for a conventional water dam using compacted, graded gravel with a layer of clay on the internal face and a rock toe for drainage on the external side. Coarse sands settling out on the beach area of the tailings pond are also used in starter dyke construction upstream. Seepage is returned to the ponds using heavy sump pumps (see p. 20). Some problems have been experienced with dust production around the edges of the ponds, and settling of the clays may be at a lower percent solids than anticipated.

According to Vogt (1976) the problem of land disposal of bauxite residue at Kaiser's two Louisiana alumina plants led to a comprehensive development program on dewatering techniques between 1970 and 1973. A sand bed filtration system was selected and is now in operation at the Kaiser Gramercy Works. This process is shown to reduce red mud slurry volumes to from one third to one fourth of the initial volume. Given the slurry characteristics and system design, the impounded mass will, upon reaching its maximum consolidation, show little tendency to repulp. Indications so far are that the impoundment area, upon stabilization at the surface, may be reused for farming (after replacing topsoil) or mining of the mud for other uses. Vogt finds that bauxite residues at about 50 percent solids will support men and equipment, and shows little tendency to flow.

In some areas, alumina plant tailings are sufficiently low in clay content that they can be dewatered to a point where they can be dumped rather than impounded in a dyked-off area. Slides have taken place at such dumps, however, and Jenny (1974) has examined the soil mechanical properties of these types of tailings as a function of fines content.

Rushing (1973) discusses problems associated with the disposal of tailings from the refining of Caribbean bauxite ore. He provides a brief review of potential uses through tailings reprocessing which, he concludes, does not show an economic or volume potential. Wasting to rivers and ocean or tailings storage on land areas are considered by him to be the present solutions for disposal. He points out that the Sherwin Alumina Plant of Reynolds Metals Co. has used land storage and has progressed from lake storage to drying beds adjacent to the plant to drying beds some 14 km (9 mi.) from the plant. Design considerations to prevent pollution at the dyked areas and for the long tailings pumping system are given.

China Clay Mine Tailings

Large scale hydraulic mining of china clay can only be seen in the counties of Devon and Cornwall in South West England. The Clay Division of English China Clays extracts 22 million tons of material per year, of which about 10% is micaceous waste. Ripley (1972) describes the methods currently employed for disposal of this waste, which is usually in dyked-off areas as a slime ranging in water content from 35% to 56%.

The deposits of kaolin, formed by the hydrothermal alteration of the feldspar minerals in the granite bosses of South West England, extend to considerable and unproven depths. The kaolin is associated with sand, other silt and clay size particles, unaltered granite, lode material of various types and overburden. The clay is mined hydraulically by high pressure bores, known as monitors. The slurry produced by the hydraulic monitors at the pit face gravitates to the lowest part of the pit where it is pumped to spiral classifiers. These remove the sand from the slurry, which is then fed onto a conveyor and carried to a tip. The slurry is pumped away for further refining and processing.

The stages of refining may be listed as follows:

- (1) Removal of sand by spiral classifiers;
- (2) removal of coarse micaceous material by hydrocyclones;
- (3) removal of fine micaceous material in settling tanks;
- (4) separation of coarser clay by centrifugation.

The micaceous waste material has been traditionally disposed of into rivers, but as a result of recent anti-pollution legislation, dispersal into lagoons is now the only available method.

The mineralogy of this micaceous waste is very variable, but in general it is composed of 50% coarse kaolinite, with the remainder being essentially muscovite and lithionite mica with small quantities of biotite mica, quartz, tourmaline, potash and sodium feldspar. Quartz forms the bulk of the non-mica material.

During the winter of 1969/70 dyke failure occurred in three tailings lagoons within a period of five weeks, and considerable attention is now being given to dyke stability in the area. The possibilities of re-working the

"mica", particularly the material deposited when separation techniques were not as effective as they are today, is being actively pursued. Clark (1974) details some of the processes that might be used in this respect. In particular he discusses fine particle flotation, when the fine particles are carried by coarser particles to which normal flotation techniques are applied. He also discusses froth drainage as a separation method, along with flotation by two immiscible liquids, differential flocculation and coagulation, and wet magnetic methods. It is possible that some of these methods may be applicable to the processing of other waste slimes, where, for instance, swelling components, such as montmorillonite or attapulgite, could be removed to provide for more ready dewatering.

Ocean disposal of clay mining wastes has also been considered. Koshti (1974) describes how large scale tests were conducted in England by English Clays Lovering Pochin and Co. to study the feasibility of discharging 2 million tonnes/annum of micaceous tailings into the sea. The investigations included hydrographic surveys; radio-active tracer evaluations; and large scale model tests. Results indicated that a white plume would appear in the area; the storage capacity was of limited life; the possibility of the formation of a mound could constitute a hazard to shipping; and there were no guarantees that particles would not be transferred back to local beaches. The disposal scheme finally adopted by this company also consists of storing the residue on land already owned by the industry, and involving the preparation of disposal areas fed by a 12 mile pipeline complex.

The deposits are fairly continuous both in grade and thickness over large areas, but locally both may change abruptly. The present mining areas are in that terrain lying 100 - 150 ft. above sea level. From 10 to 20 ft. of overburden (including the leached zone) must be removed in order to mine the matrix, which is usually 10 - 30 ft. in the areas now being mined. The ratio of overburden to matrix, as well as the grade of concentrates, largely determines the economics of mining a particular location.

All companies in the area operate with a similar mining procedure. At the mining area, the overburden is removed, typically by a 45 yd. electric drag-line (there are currently about 40 operating in the Bone Valley) and dumped into the previously mined-out area. The matrix is then mined by the same unit and dropped into a shallow pit on the surface of the ground from whence it is pumped, after slurring with high pressure water guns, to the concentration plant. The modern Florida operation consists of washer, agglomeration, and often flotation and drying plants. The product from the washer plant are pellets ranging from 1/16 to 1 in. in diameter and consisting of 15 - 85% of the total phosphate, depending upon the nature of the deposit. These coarse particles are separated from the rest of the slurry by a series of vibrating screens equipped with water sprays. The water sprays and log washer are employed to separate the phosphate from mud balls and clay. It is customary to separate the coarser phosphate pebbles from the fine ones by screening, since this is the most economical way to concentrate in the first step. The product from the agglomeration plant usually ranges from -16 to +48 mesh. To obtain particles in this size range, a reagent of fatty acids, sodium hydroxide, and fuel oil is used to selectively coat the phosphate particles, which then tend to agglomerate underwater. The particles of selectively oiled phosphate rock roll down an underwater screen, while the sand goes through the meshes of the screen.

The particles ranging from 48 to 150 mesh are called flotation concentrates. In the flotation plant, the particles of phosphate rock are again selectively oiled by the same type of mixture used in the agglomeration plant, so that the particles will attach themselves to air bubbles and rise to the surface, where they are skimmed off. The uncoated sand is discharged continuously at the bottom of the cell. By this process, a first-stage concentrate

is obtained which is deoiled with sulfuric acid and again purified by a flotation step. In the second flotation, a cationic surfactant, such as a fatty acid amine or quaternary ammonium compound, is employed with a frothing agent, such as pine oil, to float the sand away from the phosphate fines which are continuously discharged at the bottom of the cell. The final drying operation is usually carried out in large, horizontal, rotary kilns.

During the forty years or so of commercial phosphate pebble-rock recovery in Florida, there has been a problem with the disposal of clay slimes, or all material in the matrix smaller than 150 mesh. Even though these slimes contain as much as 30% of the phosphate values contained in the matrix, this is not amenable to flotation recovery. Inability to dewater is a most significant characteristic of the slimes, resulting in substantial water usage and immense disposal areas.

A review of the environmental impact of phosphate slimes in central Florida is provided in an Environmental Science and Technology feature article (Envir. Sci. Technol., 1974). Much of this information was updated and used as material in a recent discussion on the CBS newsprogram "60 Minutes" (April 10, 1977). It is estimated that there are now 45,000 acres of tailings ponds containing a total of about 15 billion gallons of liquid waste. Each tailings pond averages 400 acres in area. 30 major spills from the dyked areas have occurred since 1940, one of which recently (1971) caused fish kills in the Peace River for 85 miles downstream to Charlotte Harbour. Florida State law now requires that all dykes containing active disposal areas be inspected visually once every eight hours, and those containing inactive disposal areas about once every week. President Ford in 1976 commissioned a study by the Council on Environmental Quality to assess the environmental effect of the phosphate mining industry on Florida, since a high level of activity in this respect is expected to continue for several decades.

Phosphate slimes can have a variety of compositions, but normally consist of:

- (a) clay minerals, principally montmorillonite, attapulgite, kaolinite and occasionally illite;
- (b) phosphate minerals, mostly fine-grained carbonate-fluorapatite, with lesser amounts of aluminum phosphates,

- such as wavellite;
- (c) quartz, occurring as sand or silt-sized particles;
- (d) other minerals, such as feldspar, heavy minerals, and hydrated iron oxides, in minor amounts.

Unlike oil sands slimes, the phosphate slimes contain no significant organic material, and are at a slightly acid pH. The slimes, as produced, contain from 3 - 5% solids. They eventually settle to about 15% in something less than one year, reaching close to 20% after 10 years (Hoppe, 1976; see also p. 17).

About 50% of the slime solids are in the colloidal range, and the clay fraction in this range is responsible in large part for the high water retention of the slimes and their slow settling behavior. The predominant effect is believed to be derived from attapulgite (Lamont, 1975), a magnesium silicate clay. This clay is fibrous, expanding, and believed to contribute a "haystack" structure to the sludges, much as montmorillonite may contribute a "card-house" structure to oil sands sludges. Phosphate slimes also contain the latter, but Hoppe reports that attapulgite content has been shown to have a direct effect on the sludge dewatering rate.

A considerable literature has arisen on the subject of treatment and disposal of phosphate mine tailings. A review by the U.S. Bureau of Mines (1975) lists some 290 references to articles in the area. An update is provided by a series of papers recently published from the Florida Phosphatic Clays Research Project (Bromwell and Oxford, 1977; Keshian et al, 1977; Martin et al, 1977; Oxford and Bromwell, 1977), which was set up as a cooperative venture between representatives of the phosphate industry and the U.S. Bureau of Mines following the 1971 dyke failure. Fundamental studies on the thickening and sedimentation of slurries in general have been carried out using phosphate slimes (Smiles, 1975; Somasundaran, 1973). Somasundaran finds, for instance, that passage of coarser particles during sedimentation through a sludge is beneficial in that this promotes formation of fissures and cracks through which water may be expelled to the surface.

Because of low surface charge and mechanical hindrance between particles, attapulgite responds poorly to flocculants. Its fibrousness may be an aid in filtration, but no really practical filtering process has yet been developed. A number of dewatering techniques have, however, been proposed. The U.S.

Bureau of Mines review reports studies on gravitational thickening, hydrocycloning, centrifugation, electrical dewatering, freezing, drying and bacteriological dewatering, all of which have been found either technically or economically unsatisfactory. The article in Environmental Science and Technology also mentions that ultrasonic vibration, evapo-transpiration, magnetic separation, mechanical compression, and ultraflotation (piggy-backing on a coarser auxiliary mineral flotation carrier) have also been investigated for dewatering purposes, and have also been found to be impractical.

More recent studies include filtration in the presence of flocculant (Terichow, 1975) and dewatering by adding fly ash, polyelectrolyte and blending (Mewes, 1976, see p. 28; Bakhshi, 1974). In the latter it is claimed that the clear water supernatant may be drawn off from the sedimented solids, which can be further dewatered or treated in ecologically beneficial ways. Hardman (1975) claims a process in which dewatering the slimes is aided by disposing of them in layers up to 18 in. thick followed by occasional kneading to promote drainage and evaporation of water. After about 10% of the original water is removed from a layer, fresh slimes are added and the process repeated. Dry processing of ore, which could eliminate the production of slime wastes, although considered unfeasible up to the present time, has been investigated (Ribas, 1976).

Davidtz (1974) claims a process in which slimes are mixed with topsoil or overburden containing 200 ppm or more water extractable organic material to give a flocculated solid which is readily filtered. Hortenstine and Rothwell (1972) explore the possibilities of using municipal compost in reclaiming the tailings areas. Their results showed good plant growth if fertilizer was also added. Vasan (1972) describes a method in which phosphate slimes are converted into building materials by a fluidized drying bed. Process modification has also been considered in order to cut down on water usage and minimize disposal requirement (Oltmann, 1971).

Current large-scale slime pond reclamation efforts being carried out by the industry involve crust development and sand spray techniques (see Mougdil, 1976; Hoppe, 1976; Bromwell and Oxford, 1977). In the former case drainage of free water from the surface coupled with evapotranspiration eventually established a crust of sufficient strength to support agricultural

tractors. A key step in the operation is the initial deployment of wide tracked vehicles on the surface after some crusting to mow vegetation and establish drainage ditches. In the latter case sand is sprayed from nozzles attached to floating pipelines over settled clay slimes placed in mined-out cuts. As the sand settles through the slimes a substantial additional release of water occurs. After spraying, additional clay is placed to fill the void created by consolidation, and the process repeated. Finally, a small bucketwheel excavator and a suspended belt distribution machine are employed to cap the filled mine-cuts with overburden from the spoil banks.

Research is continuing on the use of upflow clarification after flocculant addition to achieve an approximately 18% solids content sludge, which can then be disposed of in a sandwich configuration, with clay layers alternating with sand layers to provide higher consolidation stresses (Mortin et al, 1977). Mixing sand with pre-thickened flocculated clay sludges has also been found to promote dewatering by producing higher confining stresses. Pre-thickened clays can also be obtained by natural settling, and Bromwell (1977) discusses a sequence involving dredging settled clays from an existing disposal area and mixing these with sand tailings prior to use as backfill material.

CONCLUSIONS AND RECOMMENDATIONS

The satisfactory disposal or elimination of clay slimes is a key requirement for the continued extraction of surface mined oil sands. It is possible that elimination can be accomplished by modifying or replacing the existing hot water process, and vigorous research should be continued in these areas. In the meantime, the investigation of techniques that will lead to the satisfactory abandonment of the existing ponded G.C.O.S. slimes and those that will be produced by the Syncrude and any other conventional hot water plant is still a necessary endeavor.

A primary objective of the research on phosphatic clay slimes in Florida is to remove the need for above-ground storage of the slimes behind dykes. This method of disposal has sequestered large land areas and has proved to be hazardous. Since the expansion of the industry in the 1940's, 30 dyke failures have occurred, some of which have had serious impact on the surrounding habitat. A minimum level of satisfactory abandonment for Alberta oil sands clay slimes would seem also to involve containment of these liquid tailings below grade in mined-out areas, after removal of residual bitumen. Continued slow sludge compaction would eventually turn such disposal areas into shallow lakes, and this could be acceptable in itself provided the water-sludge interface, which would constitute the lake beds, were stabilized to seal off the sludge layer and ensure reasonable water quality. If a sufficiently large number of disposal areas were to be produced it may be desirable to revegetate at least some of them and make them accessible to land animals. In either case, crust formation over the ponded slimes would be a necessary first step. Natural freeze-thaw cycles, coupled with good surface drainage, may be sufficient to accomplish this. Dewatering techniques, although prohibitively expensive if applied to the total bulk of the slimes, may also prove economically feasible for this task, and should continue to be investigated in this respect. Although some information is already available on the relationship between dewaterability and slime composition, the area should be further explored, possibly starting with synthetic clay mixtures containing varying amounts of bitumen-like materials.

Sand tailings in excess of those that could be contained in mined out areas already partially filled with clay tailings could be stored with relative safety above ground. Research in optimizing and stabilizing various configurations in this

context especially with regard to considerations such as drainage, available land area, and revegetation, could be a continuation of those studies already performed in relation to the sand tailings dykes.

Since perpetual storage in some form or other is contemplated for the slimes, detailed microbial investigations of these materials from the point of view of indigenous as well as inoculated populations, under both aerobic and anaerobic conditions, should be undertaken. These would provide a basis for the prediction and observation of biologically caused changes that may occur over the years to come. Steps could then be taken to minimize detrimental effects resulting from the production of undesirable metabolic end products, including toxic and carcinogenic compounds, should they be predicted to occur.

On the other hand, amplification of bacterial metabolism using the activated sludge process may reduce or eliminate undesirable constituents within the tailings. The process could be applied, for instance, to tailings pond drainage, perhaps in combination with upgrading plant effluent. A study of the resident bacterial population, and others that could survive in the tailings studies would provide good indication as to the feasibility of such treatment. The microbial ramifications of treating clay tailings with nutrients or domestic sewage to promote bacterial growth are as yet unknown, and also warrant close study.

Although the oil sands clay disposal problem differs in detail from the Florida phosphatic clay problem, much of the technology proposed for the former has already been investigated for the latter. With the understanding that conditions and methods of application may differ, the Florida experience provides a large source of valuable information on disposal methods which might be useful in Alberta. In particular, methods involving repulping of settled or flocculated sludge with sand tailings prior to placement in mined-out areas, and sandwich placement of alternate sand and clay tailings layers into mine pits, which seem to show promise in Florida, bear investigation in the oil sands context. Another area of research that might prove fruitful involves flocculation of clay suspensions in the presence of sand tailings immediately prior to rapid dewatering techniques, such as hydrocycloning or filtration. There is evidence that relatively high clay to water ratios may be realized in the sludges resulting from these operations. Flocculation studies in general should be carried out with a view to providing high clay/water ratio sludges rather than for

clarification purposes.

Pilot plant studies have indicated that clays will be present in the emulsions recovered by in situ oil sands extraction methods. The amounts are still uncertain, and in any case will vary with the quality of the deposits extracted. If the clays are produced in sufficient quantities that they remain with the aqueous phase after the emulsions are broken, they will need to be separated as sludges, before discharge or recycle of the aqueous stream, and stored above ground. It is likely that sludge quantities will be small, and that advanced dewatering techniques, such as those currently under investigation for kimberlite and china clay slimes, may become appropriate. The situation should be closely monitored and the necessary research efforts undertaken. These could well be integrated with research on crust formation methods for hot water process slime disposal areas. A key part of this dewatering research would be to determine target levels of solids content for different disposal configurations.

Finally, cooperative research and free exchange of information between industry, government and university research groups, in the areas of concern, would greatly expedite the satisfactory solution to environmental problems that have presented themselves in the development of the oil sands. Although considerations of proprietary rights are often a factor in precluding such an arrangement, it should be realized that, in the case of the Florida phosphate mining industry, these have become secondary in the context of the massive reclamation effort now being faced in the Bone Valley.

APPENDIX

Clay Structures

A comprehensive review of the structural aspects of the surface and colloid chemistry of clays is given by Swartzen-Allen and Matijevic (1974). An Introduction to Clay Colloid Chemistry (van Olphen, 1963) is a definitive text in the field. An excellent synopsis of clay structures is also given by Stumm and Morgan (1972), on which the following brief description is based.

Clay minerals are primarily crystalline aluminum or magnesium silicates with stacked-layer structures. Each unit layer is in turn a sandwich of silica and gibbsite or brucite sheets. In the silica or tetrahedral (T) sheet (see Fig. 3) silicon atoms are each surrounded by four oxygen atoms in a tetrahedral arrangement; these tetrahedra are connected in an open hexagonal pattern in a continuous two-dimensional array. The gibbsite or brucite layer, or octahedral (O) sheet (see Fig. 3) consists of two layers of oxygen atoms (or hydroxyl groups) in a hexagonal closest packed arrangement with aluminum or magnesium atoms, respectively, in the octahedral sites. These sheets are stacked into two - or three-layer units (T-O or T-O-T) in which the oxygen atoms at the vertices of the tetrahedra in the T-sheet also form the basic hexagonal pattern of the O-sheet (so that a T-O layer is 5 atoms thick and a T-O-T layer, 7 atoms). The unshared oxygens in the O-sheet are hydroxyl groups. Isomorphous substitution of Al(III) for Si(IV) in the T-sheet (or Mg, Fe, Zn (II) for Al(III) in the O-sheet may lead to negatively charged layers. In clay minerals, the T-O or T-O-T units are stacked one on another, with layers of water and/or interlayer or surface cations (to compensate the negative charge) between the units. These cations may be exchangeable, and interlayer water may be absorbed by a dry clay, causing it to swell.

Types and Examples:

- (a) Two-layer clays (Fig. 4)
- These clays are characterized by little isomorphous substitution, small cation exchange capacities (CEC) and are nonexpanding. Examples include kaolinite, dickite, nacrite, and halloysite (which contains interlayer water).

(b) Three-layer clays (Fig. 4)

i) Expanding (Smectites or Montmorillonites).

These are characterized by substitution of a small amount of Al for Si in the T-sheet and of Mg, Fe, Cr, Zn, Li for Al or Mg in the O-sheet. They are associated with large cation exchange capacities ($M^{m+} = Na^+, K^+, Li^+, Ca^{2+}, \dots$) and swell in water or polar organic solvents. Examples include: montmorillonite, nontronite, volkhonskyite, hectorite, saponite, sauconite, and vermiculite.

ii) Non-expanding (Illites)

In these clays about 1/4 of the Si in the T-sheet is replaced by Al, with similar substitutions as in i) in the O-sheet.

They exhibit small cation exchange capacities and are poorly crystallized. M^{m+} is K^+ , which is very strongly held. This group includes the micas (muscovite, biotite and phlogopite).

(c) Chlorites (Fig. 4)

These clays exhibit a structure in which three-layers alternate with brucite layers. The latter are positively charged, with some Al(III) replacing M(II), and partially balance the negative charge on the T-O-T, or mica, layer. They are associated with low CEC and are non-swelling.

(d) Fibrous Clays

These include different types of structural units consisting of double silica chains (tetrahedral) joined to one-dimensional O-layers and containing interstitial water. Examples are attapulgite, palygorskyite, and sepiolite.

(e) Mixed Layer Clays

Clay minerals exhibit, in addition to polymorphism due to the disordering and proxying of one element for another, intercalation, either ordered or random, of layer structures with one another. For example, sheets of illite may be interspersed with montmorillonite, or chlorite with one of the others, either randomly, or regularly, producing what is called mixed-layer clay minerals.

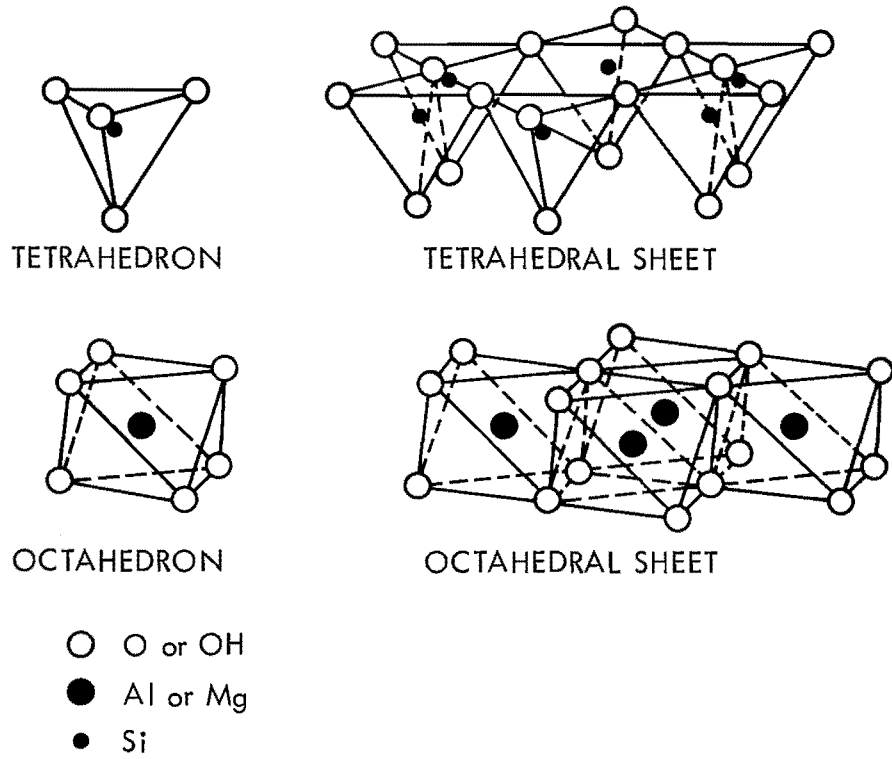
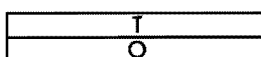
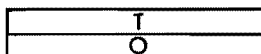
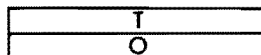


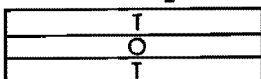
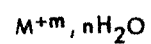
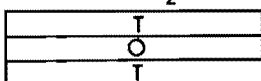
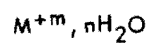
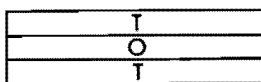
FIGURE 3: T AND O SHEETS IN CLAY STRUCTURE

Structure

A. Two-Layer Clays



B. Three-Layer Clays



C. Chlorites

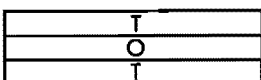
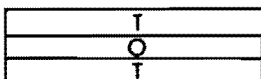


FIGURE 4: Clay Structures

Matijevic (1972, 1974, 1975, 1976) has also published a series of papers which report on the surface and colloidal properties of various natural (montmorillonite, kaolinite) and synthetic (laponite) clays. Experimental techniques that are described include coagulation studies involving measuring capillary suction time and turbidity, studies of the adsorption of multivalent and chelate ions by radiotracer techniques, and electrophoretic mobility studies over a range of pH and in the presence of various counter ion species. Stability of the clay suspensions is discussed in terms of the particle surface configurations and charge. Rand and Melton (1975) have reported evidence that the isoelectric point of the edge surface of kaolinite occurs at pH ca. 7.3. They hypothesize that at this pH a kaolinite/water suspension is flocculated in an edge-to-edge structure at all ionic strengths and that edge-face (card house) structures are only possible below this value at low ionic strengths. On the other hand, Kitchener (1974) convincingly argues that coagulation of clays by the addition of salts results in a very open "card-house" structure in which edge-to-edge collisions produce permanent contact, face-to-face contacts are virtually excluded and face-to-edge coagulation proceeds with an intermediate probability.

Clay Interactions With Other Materials

Graham (1964) has published a review on clay-water interaction and the structural characteristics of the adsorbed water. The review includes a discussion of the behavior of adsorbed water when a clay gel is frozen. Interlayer water does not freeze to ice, although solidification of some form appears to become completed when temperatures of the order of -100°C are reached. Davis and Worrall (1971) describe a method by which the adsorption of water on clay surfaces can be determined by "negative" adsorption of glucose from aqueous solution. The measured thickness of adsorbed water for kaolinites was found to be of the order of a few hundred Angstroms, of which 15 \AA consisted of rigidly bound water with the remainder existing as "flickering clusters". For montmorillonites the thickness of the water film, both internal and external, was found to be less than on kaolinites. This was ascribed to structural and spatial restrictions. Although the measured adsorption depended on the initial glucose concentration, it was found possible to extrapolate the results to zero concentration. Water adsorption was found to be strongly dependent on the nature of the exchangeable cations, i.e. whether they were structure-breakers or structure-formers, and was suppressed by high electrolyte concentrations. Anderson (1973) has carried out several investigations into the behavior of clay-water systems on freezing. He has shown that every freeze-thaw cycle results in a redistribution of water within porous media, and that if a medium is unconsolidated or compliant, particle movement and reorientation or deformation of the matrix is a result. In general, he has found that the more slowly a cycle is traversed, the greater is the effect. During the cooling portion, water migrates to sites of ice nucleation and adds to the enlarging crystals until an equilibrium between ice and the remaining unfrozen interfacial or capillary water is reached. On warming, progressive melting releases water that then is free to permeate the matrix. Experimental observations indicate freezing and thawing can provide channelling in this manner. The importance of channelling in sludge dewatering has been described in other studies (p. 66, Dell, 1971; p. 51, Somasundaran, 1973). Anderson has also found the unexpected result that at equilibrium on freezing, kaolinite retains a larger quantity of unfrozen water than montmorillonite.

Theng (1972) has published a review in which he summarizes the development of and advances in the chemistry of clay-organic reactions. A brief outline is given of the structural features of clays and those peculiarities of the mineral surface that influence their behaviour towards organic compounds. He discusses the formation and properties of the different types of clay-organic complex, including some examples of the practical application of the clay-organic interaction. Of particular note are the sections on the intercalation of organic molecules and ions, the formation of charge-transfer complexes and the interaction of clay particles with water-soluble polymers in aqueous systems. Birkner and Edzwald (1969) found that adsorption of a non-ionic polymer, polyethylene oxide, onto kaolinite follows Langmuirian type behaviour. This is consistent with a model in which the polymer molecule segments displace water molecules adsorbed on the surface of the clay particles. Results concerning the effect of pH and of solution cation type on the adsorption are considered to support a model in which hydrogen bonding occurs between the methylene groups in the polymer chain and oxygen atoms in the clay surface. AlO^- and SiO^- groups are considered to be important contributors to the latter, and it is from here that the pH and ion effects are believed to be derived, i.e. reduction in pH can protonate these groups and make them less available for hydrogen bonding. The use of fatty acid soaps to float clay impurities away from titanium dioxide is described in a patent claimed by Weir (1972). Friberg et al (1974) discuss the influence of interactions between hydrolyzed aluminum ions and polyacrylamides on the sedimentation of kaolin suspensions. They suggest that the positively charged hydrolyzed metal ions act as "anchor points" to attach the negatively charged polyacrylamides to the negatively charged clay particle surfaces. Le Bell et al (1976) have studied the influence of sodium lignosulphonates on the stability of kaolin suspensions by determining the critical coagulation concentrations of sodium chloride for the suspensions with varying amounts of lignosulphonate added. Clementz (1976) has studied the adsorption of asphaltenes and resins onto montmorillonite, which he found to occur rapidly and essentially irreversibly under near-anhydrous conditions. Factors which influenced the adsorption were the exchangeable cation on the clay, the basic nitrogen components of the molecules, and the solvent. X-ray powder diffactograms showed that some interlamellar penetration of the clay had occurred,

with the layers being visualized as "propped" open by the partial interlayer penetration of the adsorbed heavy ends. As a result of this adsorption, the physical and chemical properties of the clay were found to be drastically altered. For instance, the montmorillonite became quite hydrophobic and did not disperse readily in distilled water. The physical and chemical behaviour of clays in petroleum reservoirs are discussed in the light of these findings.

Secondary recovery of a petroleum deposit involves the injection of water to displace oil from the reservoir. High injection rates are generally desired, and in some cases the flood will not be economic unless high rates are maintained. The presence of clays which swell in contact with water offers a complication to the problem of maintaining adequate injectivity. Slobod and Beiswanger (1968) have found that certain nonionic and anionic polymers have the abilities to reduce this swelling, and were found effective in controlling clays present in Berea sandstone cores. A method of treating a formation containing water sensitive clays to prevent swelling is claimed by Thompson (1973). In this method the formation is first treated with alcohol which will not appreciably swell or disperse the clays. The formation is then contacted with phosphoric acid or phosphorus pentoxide, dispersed in a similar alcohol, for a sufficient period of time to stabilize the clay minerals.

Kendall (1974) discusses problems associated with swelling-clay formations which must be drilled through to reach the underlying petroleum deposits in the Norwegian sector of the North Sea. The hole making is itself rapid, but the clay cuttings can blind shaker screens and lead to the production of clay rings around the drill pipe and clay balls in the drilling mud. Time consuming clean-out operations then become necessary. Chemical measures can be taken to reduce the degree of swelling of the clays. A major reduction in swelling can be accomplished by incorporating potassium ion in the drilling mud, which can exchange with sodium or calcium ions in the clay. The potassium ion is of such size and charge density that it promotes formation of a closed structure when held between the two hexagonal tetrahedral sheets that contact each other in the building of a three-layer clay (see also p. 19, van Olphen, 1963). Kendall also refers to an organo-aluminum compound which is said to adsorb onto the clay through secondary valence forces available in the complex and prevent hydration.

Hudson and Braden (1974) have patented a method by which clays in underground formations are desensitized to water swelling by treatment with solutions which accomplish electrodeless deposition of metal on the clay particles. The economic feasibility of such a process is not discussed.

Characteristics of Clay Floccs

Gibson and Hussey (1967) discuss the theory of one-dimensional consolidation of saturated clays. Their approach assumes that D'Arcy's law is valid, although they recast it in a form in which it is the relative velocity of the soil skeleton and the pore fluid that is related to the excess pore fluid pressure gradient. Dollimore and Horridge (1972) studied the flocculation behavior of china clay-polyacrylamide suspensions by measuring the sedimentation rate, final settled volume of the floccs, turbidity of the supernatant and filtration rate through the settled floccs. They concluded that the optimum polymer concentration for effective flocculation is determined by the rate of fall of the floccs and the rate of filtration through the settled floccs.

Dell and Keleghan (1973) demonstrated that slow stirring can have beneficial effects on the dewatering of clays flocculated with long chain polyelectrolytes (referred to as "polyclay" systems). The stirring was shown to provide an easy escape route for the water as well as to remove frictional support from the walls of the vessel in which the flocculated sludge had settled. They propose a three-regime physical model for the thickening of such flocculated systems. Ferreiro and Helmy (1974) studied the flocculation of Na-montmorillonite by three different electrolytes, and found the ratio of the flocculation values of the different salts to be in reasonable agreement with that predicted by the Derjagin-Landau and Verwey-Overbeek theory of colloid stability. Wright and Kitchener (1975) determined permeability and strength as functions of solids content for flocculated sludges of the swelling clays laponite and sodium montmorillonite. They discuss the implications of the results for optimizing the dewatering of swelling clay sludges by filtration.

Dell (1970) describes the use of deep cone thickeners for the dewatering of flocculated coal washery tailings. Dell (1971) also reviews research on the compaction behavior of clay sludges resulting from the flocculation of coal washery tailings. It appears that such flocculated systems consist of two distinct zones, an upper undisturbed zone and a lower, channelled zone, the latter building up progressively with time. The channels were considered potentially important in the practical problem of rapidly and easily removing water from flocculated clay. The theoretical implication of this phenomenon

was considered to be that, since channels have such a profound effect in reducing the specific resistance of flocculated clays, the rate of passage of water through an element of solid depends mainly on the extent to which the element is channelled, and not on the overall concentration of solids in the element.

Drilling Muds

Drilling fluids are often based on deliberately stabilized clay suspensions. As such, they have many characteristics in common with the slimes produced by the settling of clay tailings, and they illustrate many interesting facets of the physical and chemical aspects of clay surfaces.

A drilling fluid is required to

- (1) lift cuttings from the bore;
- (2) control well pressures, and
- (3) cool the bit.

In particular, the removal of rock chips from the cutting face of the bit and the transport of those cuttings to the surface are dependent on the flow properties of the drilling fluid as well as the velocity of its movements. The filtration properties of drilling muds are also important, in that they provide a measure of the ability of the solid components of the muds to form a thin, low-permeability filter cake. The lower the permeability, the thinner the filter cake and the lower the volume of filtrate from muds of comparable solids concentration. This property is dependent upon the amount and physical state of the colloidal material in the mud. It has been shown repeatedly in the field that when mud of sufficient colloidal content is used, drilling difficulties are minimized. In contrast, a mud low in colloids and high in inert solids deposits a thick filter cake on the walls of the hole. A thick filter cake restricts the passage of tools and allows an excessive amount of filtrate to pass into the formation, thus providing a potential cause of caving.

Water-base drilling fluids are the earliest known and still most commonly used drilling fluids. They are usually referred to as "drilling muds" or "muds". Depending upon the salinity of the water phase, they are called "freshwater muds" or "saltwater muds". Barite (barium sulfate) to control density, and swelling clays, to control rheology, are the major components of these muds. Other components are essentially formation solids, such as shale, anhydrite, gypsum, dolomite, limestone, sand, and salt. Salt and gypsum may be added to obtain certain desired properties in the drilling fluids. Hydrophilic chemicals, both solid and liquid, are added to adjust and control viscosity, gelation, filtration, and corrosion; counteract contaminants; stabilize emulsions;

stop loss of circulation, etc.

One of the earliest materials used to thicken freshwater base drilling muds in a controlled manner was Wyoming bentonite, a clay which contains a high amount of sodium montmorillonite. Bentonite continues to be the most widely used material in this respect. Attapulgite is used almost exclusively to thicken saltwater base drilling fluids.

Many organic materials are added to drilling mud to alter its properties, and the interaction of these materials with the clay is of direct consequence in this respect. Polyelectrolytes, such as sodium carboxymethyl cellulose and sodium polyacrylates are often added as "extenders" to increase either the plastic viscosity or the yield point. In the latter case direct interaction with the particles in a bridging mode is implied. Tannins and ligno-sulfonates, on the other hand, are added as thinners. Other thinners include inorganic clay deflocculants, such as the condensed phosphates. Since these hydrolyse, they are only preferred over the more stable organic materials in freshwater muds for shallow holes.

On the other hand, materials have been added to drilling muds to prevent formation clay swelling. These include sodium nitrate, calcium nitrate, calcium chloride, zinc chloride, sodium silicate, sodium hydroxide, lime and cement, sodium methyl silicate, polyoxyethylene sorbitol, nonyl phenol, and nonylphenolpolyethoxyethanols (Kirk - Othmer, 1963).

The drilling mud is continuously recirculated through a pit in which the transported cuttings are settled out. On completion of the drilling operation the pit is usually abandoned with usually no particular efforts taken to stabilize the mud. The volume is in any case comparatively small. Any techniques developed to consolidate the mud would, however, have application in the treatment of other clay slimes.

REFERENCES

- Alberta Department of Environment (1973). Syncrude criteria.
- Alberta Department of Federal and Intergovernmental Affairs (1974). The Alberta Oil Sands Story, Jan. , 44 pp.
- Alberta Environment (1973). An Environmental Study of the Athabasca Tar Sands, prepared by Intercontinental Engineering of Alberta Ltd. , March, 112 pp.
- Alberta Environment (1976). Spent oil-sand fertility study. April, 32 pp.
- Alberta Environment (1976). Great Canadian Oil Sands dyke discharge water. Summary report of the Scientific Enquiry Committee. August, 11 pp.
- Alberta Environment (1977). Report on the Great Canadian Oilsands Tar Island tailings dyke, by the Design Review Panel, Feb. , 191 pp. plus attachments.
- Alberta Oil Sands Environmental Research Program (1975). First Annual Report sponsored jointly by Alberta Environment and Environment Canada. 58 pp.
- Allen, A. R. (1976). Coping with the oil sands. Chemtech 6, pp. 384 - 391.
- Allen, A. R. , and Sanford, E. D. (1974). The Great Canadian Oil Sands Operation, Alberta Research Council. IS 65, pp. 103 - 121.
- Anderson, D. M. , Trice, A. R. , and Banin, A. (1973). The water-ice phase composition of clay-water systems. I. The kaolinite-water system. Soil Sci. Soc. Amer. Proc. 37, pp. 819 - 822.
- D'Appolonia, E. , and Gormley, J. T. , (1972). Abandonment of tailing facilities, in Tailing Disposal Today, Proc. 1st Int. Tailing Symp. , Tucson, Ariz. , Nov.
- Ashton, J. E. , and Davitt, H. J. (1976). Method of storing sludge recovered from hot water extraction of bitumen from tar sands. U.S. Patent 3,951,800, Apr. 20. To Great Canadian Oil Sands Ltd.
- Baillie, R. A. (1968). Process for recovering a clarified effluent from the discharge of a hot water process treatment of bituminous sand. U.S. Patent 3,392,833, July 16. Also issued as Canadian Patent 824,968, Oct. 14, 1969 under the title: Filtering tar sand residual water. To Great Canadian Oil Sands Ltd.

- Baillie, R. A. , and Malmberg, E.W. (1969). Removal of clay from the water streams of the hot water process by flocculation.
U.S. Patent 3,487,003, December 30.
To Great Canadian Oil Sands Ltd.
- Baillie, R. A. (1970). Effluent discharge bitumen recovery.
Canadian Patent 841,582, May 12.
To Great Canadian Oil Sands Ltd.
- Baillie, R. A. , and Fear, J.V.D. (1976). Method of reducing sludge accumulation from tar sands hot water process.
U.S. Patent 3,931,006, Jan. 6. Also issued as
Canadian Patent 965,364, Apr. 1, 1975.
To Great Canadian Oil Sands Ltd.
- Baillie, R. A. , and Fear, J.V.D. (1976). Method of reducing sludge accumulation from tar sands hot water process.
U.S. Patent 3,933,318, Apr. 27. Also issued as
Canadian Patent 976,102, Oct. 14, 1975.
To Great Canadian Oil Sands Ltd.
- Bakhshi, N.N. , Gillies, R.G. , and Khare, P. (1975). Treatment of tar sands tailings with fly ash. *Envir. Sci. Technol.* , 9, pp. 363 - 364.
- Ball, M.W. (1941). Development of Athabasca Oil Sands, *Can. Inst. Min. Metall.* , 64, pp. 58 - 91.
- Baptista, M.V. , and Bowman, C.W. (1969). The flotation mechanism of solids from the Athabasca Oil Sands, 19th Can. Chem. Eng. Conf. , Edmonton, October.
- Barr, F.T. , et al (1964). Inclined rotary drum extraction of tar sands.
Canadian Patent 687,554, May 26.
To Esso Research and Engineering Co.
- Baswick, S.D. (1976). Ultrasonic separation of bitumen from oil sands.
Canadian Patent 996,485, Sept. 7.
No assignee.
- Baugh, J. E. , and McClennon, L.L. (1976). The future of oilsands mining projects. 26th Can. Chem. Eng. Conf. , Toronto, paper 8d.
- Bell, A.V. (1974). The tailings pond as a waste treatment system. *Can. Mining and Metallurgical Bulletin*, Apr. , pp. 1 - 6.
- Bell, A.V. (1975). Some recent experiences in the treatment of acidic, metal-bearing mine drainages. *Can. Inst. Mining Metallurgy Bull.* , 68, pp. 39 - 68.
- Berkowitz, N. , and Speight, J.G. (1975). The Oil Sands of Alberta. *Fuel*, 54, pp. 138 - 149.

- Berry, C.B., and Klym, D.J. (1974). Reclamation of mined land, Great Canadian Oil Sands Ltd. lease site, Tar Island, Alberta. Workshop on Reclamation of Disturbed Lands in Alberta, Edmonton, March 27 - 28.
- Birkner, F.B., and Edzwald, J.K. (1969). Non-ionic flocculation of dilute clay suspensions. *J. Amer. Wat. Wks. Ass.* 61, pp. 645 - 665.
- Bjerrum, L., et al (1967). Application of electroosmosis to a foundation problem in Norwegian quick clay. *Geotechnique*, 17, pp. 214 - 235.
- Bowman, C.W. (1967). Molecular and interfacial properties of Athabasca Tar Sands. *Proc. 7th World Petrol. Congr.*, V.3
- Boyle, F.A. (1959). Treatment of underground formations. U.S. patent 2,908,641, Oct. 13. To Sun Oil Co.
- Bromwell, L.G., and Oxford, T.P. (1977). Waste clay dewatering and disposal. ASCE Specialty Conference, Geotechnical Practice for Disposal of Solid Waste Materials, Ann Arbor, June.
- Camp, F.W. (1970). Removing suspended solids from a liquid. U.S. Patent 3,526,585, Sept. 1. To Great Canadian Oil Sands Ltd.
- Camp, F.W. (1971). Hot water process improvement for reducing fresh water requirement. Canadian Patent 882,668, Oct. 5. To Great Canadian Oil Sands Ltd.
- Camp, F.W., and Baillie, R.A. (1972). Regulating the water input in the hot water process. Canadian Patent 890,903, Jan. 18. To Great Canadian Oil Sands Ltd.
- Camp, F.W. (1973). Increasing the operable clay to water ratio in a hot water process for separating bitumen from tar sands. Canadian Patent 918,590, Jan. 9. To Great Canadian Oil Sands Ltd.
- Camp, F.W. (1976). The Tar Sands of Alberta, Canada. 3rd ed., Cameron Engineers Inc., Denver, Colorado, 82 pp.
- Camp, F.W. (1976). Processing Athabasca Tar Sands. Tailings disposal. 26th Can. Chem. Eng. Conference. Toronto, Oct., paper 9a.
- Can. Envir. Law. News. (1975). Environmental group threatens law suit of Syncrude air emissions. 4, Dec., p. 226.

- Canadian Institute of Mines, Petroleum Society, 28th Annual Technical Meeting,
The Canada-Venezuela Oil Sands Symposium, May 27 - June 6,
1977.
- Canadian Petroleum (1973). Syncrude Canada modified Mildred Lake scheme.
14, 11, pp. 28, 29.
- Canadian Petroleum (1974). Current oil sands production methods gulp and
pollute too much water. Sept., pp. 37 - 38.
- Carrigy, M. A. (1974). The future of the Alberta Oil Sands. Proc. of 19th
Ann. Conf. of Can. Techn. Asphalt Assoc., Regina, 19,
pp. 195 - 197.
- Chaston, I.R.M., and Forsdyke, C. (1975). Full scale testing of centrifuge
separation for use in slime tailings disposal. J. S. Afr. Inst.
Min. Metall., 76, Spec. Iss. Oct., pp. 89 - 93.
- Clark, N.O. (1973). Processing and disposal of mineral slimes. Proc. 10th
Int. Miner. Process. Congr., London, Apr. 2 - 6.
- Clementz, D.M. (1976). Interaction of petroleum heavy ends with
montmorillonite. Clays and Clay Min. 24, 312 - 319.
- Cook, F.D. (1977). Private communication.
- Cottrell, J.H. (1963). Development of an anhydrous process for oil sand
extraction, Proc. Athabasca Oil Sands Conf., Sept., p. 193.
- Cymbalisty, L.M.O. (1974). Two stage separation system.
U.S. Patent 3,847,789, Nov. 12.
To Canada-Cities Service Ltd. et al.
- Cymbalisty, L.M.O. (1975). Treatment of middlings stream from hot water
process for recovering bitumen from tar sand.
U.S. Patent 3,864,251, Feb. 4.
To Canada-Cities Service Ltd. et al
- Dalby, R.N. (1976). Oil sands development - who's next. Can. Inst. Min.
Bull. 69, pp. 83 - 85.
- Davidtz, S.C. (1976). Flocculation of phosphate slimes.
U.S. Patent 3,956,119, May 11.
To Mobil Oil Corp.
- Davis, G. A., and Worrall, W.E. (1971). The adsorption of water by clays.
Bull. Dept. Ceramics, Houldsworth Sch. Appl. Sci., Univ. of
Leeds, pp. 71 - 75.

- Davitt, J.H. (1975a). Recovery of bitumen from settling cell tailings of hot water process.
Canadian patent 970,310, July 1.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975b). Hydrocyclone treatment of middlings from hot water settling zone.
Canadian Patent 971,124, July 15.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975c). Hot water extraction and hydrocyclone treatment of tar sands.
Canadian patent 970,308, July 1.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975d). Oil recovery from tar sands using hydrocyclones and gravity settling.
Canadian Patent 970,309, July 1.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975e). Recovery of bitumen from sludge resulting from hot water extraction of tar sands.
Canadian Patent 975,699, Oct. 7.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975f). Recovery of bitumen from sludge resulting from hot water extraction of tar sands.
Canadian Patent 975,698, Oct. 7.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975g). Recovery of bitumen from sludge resulting from hot water extraction of tar sands.
Canadian Patent 975,700, Oct. 7.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975h). Recovery of bitumen from sludge resulting from hot water extraction of tar sands.
Canadian Patent 975,697, Oct. 7.
To Great Canadian Oil Sands Ltd.
- Davitt, J.H. (1975i). Recovery of bitumen from sludge resulting from hot water extraction of tar sands.
Canadian Patent 975,696, Oct. 7.
To Great Canadian Oil Sands Ltd.
- Dean, K.C., and Havens, R. (1973). Methods and costs for stabilizing tailings ponds. Min. Congr. J., 59, n12, pp. 41 - 46.
- Dell, C.C., and Keleghan, W.T.H. (1970). Compressibility of flocculated clay sediments. Filtr. Sep. 7, pp. 419 - 420.

- Dell, C.C. (1971). Laboratory studies on the removal of water from clays by deep cone thickening. *Brit. Ceramic Soc. Trans.* 69, pp. 217 - 220.
- Dell, C.C., and Keleghan, W.T.H. (1973). The dewatering of polyclay suspensions. *Powder Technology* 7, pp. 189 - 204.
- Dollimore, D., and Horridge, T.A. (1972). The optimum flocculant concentration for effective flocculation of china clay in aqueous suspension. *Water Res.* 6, pp. 703 - 710.
- Duncan, D.W. (1972). Environmental problems associated with the disposal of mining and milling waste. *West. Miner*, 45, n9, pp. 14 - 16.
- Djingheuzian, L.E. (1951). Cold-water method of separation of bitumen from Alberta bituminous sands. *Proc. Athabasca Tar Sands Conf.*, Sept., p. 185.
- Djingheuzian, L.E. (1953). Tailing disposal problems of Alberta tar sands. *Can. Mining J.*, 74, pp. 69 - 75.
- Elliott, O.M. (1975). Freeze-thaw separation of solids from tar sands extraction effluents.
Canadian Patent 973,500, Aug. 26. Also issued as
U.S. Patent 3,751,358, Aug. 7, 1973.
To Great Canadian Oil Sands Ltd.
- Environmental Health Services Divn., Govt. of Alberta (1970). Athabasca River oil spill, June, 24 pp.
- Environmental Protection Agency, United States (1973). Processes, procedures and methods to control pollution from mining activities.
Report No. EPA 430/9-73-011.
- Environmental Science and Technology (1974). Feature article "Those nasty phosphatic clay ponds", 8, n4, Apr., pp. 312 - 313.
- Fear, J.V.D., and Camp, F.W. (1972). Acoustic clarification of hot water process effluent.
Canadian Patent 890,904, Jan. 18.
To Great Canadian Oil Sands Ltd.
- Ferreiro, E.A., and Helmy, A.K. (1974). Flocculation of Na-montmorillonite by electrolytes. *Clay Miner.*, 10, pp. 203 - 213.
- Flintoff, B.C., and Plitt, L.P. (1976). The electrophoretic clarification of colloidal suspensions. *Can. Metall. Quarterly*, 15, pp. 235 - 242.

- Flock, D.L., and Tharin, J. (1975). Unconventional methods of recovery of bitumen and related research areas particular to the oil sands of Alberta. *J. Can. Petrol. Technol.*, July - Sept., pp. 17 - 27.
- Flynn, P.C., Porteous, K.C., Seyer, F.A., and Sulzle, R.K. (1975). Processing Options for Athabasca Tarsands: Implications of a Heat and Mass Balance for the Direct Coking of Athabasca Tar Sands. 25th Can. Chem. Eng. Conference, Montreal, Nov.
- Roberts, K., Kowalewska, J., and Friberg, S. (1974). The influence of interactions between hydrolyzed aluminum ions and polyacrylamides on the sedimentation of kaolin suspensions. *J. Colloid Interface Sci.*, 48, pp. 361 - 365.
- Gewers, C.W. (1968). Colloid and surface chemical problems in non-conventional heavy oil recovery. *J. Can. Petroleum* 7, pp. 85 - 90.
- Gibson, R.E., and Hussey, M.J.L. (1967). The theory of one-dimensional consolidation of saturated clays. *Geotechnique* 17, pp. 261 - 273.
- Goforth, R.R., Schutte, R., and Trevoy, L.W. (1976). Development of the heavy minerals potential from the Athabasca Tar Sands, GAC - MAC Meeting, Edmonton, May.
- Graham, J. (1964). Adsorbed water on clays, *Rev. Pure Appl. Chem.*, 14, pp. 81 - 90.
- Gray, D.H., and Mitchell, J.K. (1967). Fundamental aspects of electroosmosis in soils. *J. Soil Mech. and Found. Div. ASCE*, 93, pp. 209 - 236.
- Gray, D.H. (1970). Electrochemical hardening of clay soils, *Geotechnique* 20, pp. 81 - 93.
- Gray, G.R. (1974). The Syncrude project: an engineering challenge. 24th Can. Chem. Eng. Conf., Toronto.
- Gray, G.R. (1976). The Syncrude project - year minus 2. 26th Can. Chem. Eng. Conf., Toronto, paper 8c.
- Great Canadian Oil Sands Limited (1972). Application to amend approval No. 540 with respect to tailings disposal, to Province of Alberta, Energy Resources Conservation Board. July 20.
- Great Canadian Oil Sands Limited (1974). Tailings/sludge disposal problem. Statement of problem, Jan.
- Great Canadian Oil Sands Ltd. (1976). Statement prepared in response to a press release issued on or about 13 May 1976 by the S.T.O.P.

organization, May 20. 30 pp.

- Hardman, G.J. (1975). Treatment of phosphate slimes.
U.S. Patent 3,880,703, Apr. 29.
No assignee.
- Hardy, R.M. (1974). Tailings dams, 1st Reg. Conf. Western Reg., Eng.
Inst. of Canada, Edmonton, Apr.
- Hartman, F.H. (1966). Beneficiation of Athabasca Tar Sand tailings, Can.
Dept. of Mines and Tech. Surveys, Mines Branch Inv. Rep.
IR 66-38, Apr.
- Hendry, R.D. (1974). Tar sands mining process.
U.S. Patent 3,799,613, Mar. 26.
To Canada-Cities Service Ltd. et al.
- Hepler, L.G. (1977). Personal communication.
- Hepp, P.S., and Camp, F.W. (1970). Treating hot water process discharge
water by flocculation and vacuum precoat filtration.
U.S. Patent 3,502,575, Mar. 24.
To Great Canadian Oil Sands Ltd.
- Hoppe, R.W. (1976). Phosphates are vital to agriculture -- and Florida mines
for one-third the world. Eng. Min. J., 177, n5, May, pp. 79-89.
- Hortenstine, C.C., and Rothwell, D.F. (1972). Use of municipal compost in
reclamation of phosphate-mining sand tailings. J. Environ.
Qual., 4, pp. 415 - 418.
- Hrudey, S.E. (1975). Characterization of wastewaters from the Great Canadian
Oil Sands bitumen extraction and upgrading plant. Rep. no. EPS
5-NW-WP-75-6, Environment Canada, Sept.
- Hudson, J.O., and Seitzer, W.H. (1971). Treating the process waters from
the hot water process for extracting tar sands.
Canadian Patent 878,656, Aug. 17.
To Great Canadian Oil Sands Ltd.
- Hudson, P.E., and Braden, W.B. (1974). Treatment of an underground
formation.
U.S. Patent 3,796,263, Mar. 12.
To Texaco, Inc.
- Humphreys, R.D. (1973). GCOS - Tar Sands pioneer. 24th Ann. Tech. Mtg.
of Petrol. Soc. of CIM, Edmonton. 10 pp.
- Jenny, F.C. (1974). Ferrosilt (Red Mud): geotechnical properties and soil
mechanical considerations. Metall. Soc. AIME, TMS Pap.
n A74-73, pp. 801 - 811.

- Jobson, A.M. (1976). Unpublished results.
- Jobson, A.M., Westlake, D.W.S., and Cook, F.D. (1976). Unpublished results.
- Kendall, H.A., and Norton, P. (1974). Clay mineralogy and solutions to the clay problems in Norway. *J. Petrol. Tech.* 1, pp. 25 - 32.
- Keshian, B., Ladd, C.C., and Olson, R.E. (1977). Sedimentation - consolidation behavior of phosphatic clays. ASCE Specialty Conference, Geotechnical Practice for Disposal of Solid Waste Materials, Ann Arbor, June.
- Kirk-Othmer Encyclopaedia of Chemical Technology (1963). 2nd ed., J. Wiley and Sons, New York.
- Koshti, A.K. (1975). Disposal of micaceous residues and a study of their discharge into the sea. *Proc. of 7th Mid-Atl. Ind. Waste Conf.*, Philadelphia, Nov., pp. 81 - 103.
- O'Gorman, J.V., and Kitchener, J.A. (1974). The flocculation and dewatering of kimberlite slimes. *Int. Jour. Min. Proc.* 1, pp. 33-49.
- Kramers, J.W., and Brown, R.A.S. (1975). Survey of heavy minerals in the surface mineable area of the Athabasca oil sands deposit. *Ann. West. Meeting of CIM*, Edmonton, October.
- Kruyer, J. (1977). Alberta Research Council. Personal communication.
- Kupchanko, E.E. (1968). Preliminary compatibility studies of GCOS sand tailings pond water with Athabasca River, Alberta Environ. Health Services Division Report, June.
- Lamont, W.E., McLendon, J.T., and Clements, L.W. Jr. (1975). Characterization studies of Florida phosphate slimes. U.S.B.M. RI 8089.
- Lang, W.J., and Hentz, D.A. (1973). Process for flocculating oil and clay containing slimes. U.S. Patent 3,723,310, Mar. 27. To International Minerals and Chemical Corp.
- LeBell, J.C., Hurskainen, V.T., and Stenius, P.J. (1976). The influence of sodium lignosulphonates on the stability of kaolin dispersions. *J. Colloid Interface Sci.*, 55, pp. 60 - 63.
- Libor, O. (1972). Process for the concentration of the solid content of aqueous suspensions containing clay minerals. Canadian Patent 914,925, Nov. 21. To Simonacco Ltd., Carlisle, England.

- Lulman, P. (1974). Reclamation in tar sands development - initial information and projected concerns. 4th Ontario Cover Crop Committee Conf., Guelph.
- Maloney, R.P. (1976). Spherical agglomeration method of clarifying pond water.
Canadian Patent 982,966, Feb. 3.
To Great Canadian Oil Sands Ltd.
- Massey, D.L. (1970). Stabilization of a Great Canadian Oil Sands Ltd. tailings material by use of a vegetative cover. A growth room study, Alberta Dept. of Agriculture.
- Massey, D.L. (1972). Tailings sands to trees. Published by Alberta Dept. of Agriculture.
- Martin, R.T., Bromwell, L.G., and Sholine, J.H. (1977). Field tests of phosphatic clay dewatering. ASCE Specialty Conference, Geotechnical Practice for Disposal of Solid Waste Materials, Ann Arbor, June.
- Matijevic, E. (1972). Stability of lyophobic colloids in the presence of metal chelates and chelating agents. *Kolloid Z. u. Z. Polymere*, 250, pp. 645 - 653.
- Perkins, R., Brace, R., and Matijevic, E. (1974). Colloid and surface properties of clay suspensions. I. Laponite CP. *J. Colloid Interface Sci.* 48, pp. 417 - 426.
- Swartzen-Allen, S.L., and Matijevic, E. (1974). Surface and colloid chemistry of clays. *Chem. Rev.*, 74, pp. 385 - 400.
- Swartzen-Allen, S.L., and Matijevic, E. (1975). Colloid and surface properties of clay suspensions. II. Electrophoresis and cation adsorption of montmorillonite. *J. Colloid Interface Sci.*, 50, pp. 143 - 153.
- Swartzen-Allen, S.L., and Matijevic, E. (1976). Colloid and surface properties of clay suspensions. III. Stability of montmorillonite and kaolinite. *J. Colloid Interface Sci.*, 56, pp. 159 - 167.
- Matthew, F.L. (1972). Pros and cons of combined treatment of mining and domestic wastes. In *Tailing Disposal Today*, Proc. 1st Int. Tailing Symp., Tucson, Ariz., Nov.
- Mewes, A.R., Styron, R.W., and Smith, M.H. (1976). Treatment of mineral slimes.
U.S. Patent 3,932,275, Aug. 29.
To AMAX Resource Recovery Systems Inc.

- Miners, K. A. (1972). Alcan's experience with disposal of red mud tailings from the Bayer ore process, in "Tailings Disposal Today", Proc. of 1st Int. Tailings Symp., Tucson, Ariz., Nov.
- Mittal, H.K., and Morgenstern, N.R. (1975). Parameters for the design of tailings dams, Can. Geotech. J., 12, pp. 235 - 261.
- Moore, R.G., et al (1975). Anhydrous extraction of hydrocarbons from oil sands. Instrument Society of America, Calgary Sect. Ann. Mtg., Calgary, April.
- Morley, L. A., and Parry W.T. (1971). Electroosmosis in mining. Trans. Amer. Soc. Min. Eng. 250, pp. 296, 297.
- Moschopedis, S.E., Fryer, J.F., and Speight, J.G. (1977). Water soluble constituents of Athabasca bitumen. Fuel, 56, pp. 109, 110.
- Mougdil, B.M. (1976). Mined land reclamation by the Florida phosphate industry, Trans. Soc. Min. Eng. AIME, 260, n2, June, pp. 187 - 191.
- Mrost, M. (1974). Slime disposal at South African Gold Mines. J. S. Afr. Inst. Mining Met., 74, pp. 285 - 291.
- Northern Environmental Consultants Ltd., (1975). Comments and observations upon the major deficiencies in Syncrude Canada Ltd., Environmental Impact Assessment, vols. 1 - 4. Report prepared for the Official Opposition, Alberta Legislature, Nov.
- Oilweek (1974). New generation of nuclear devices proposed for Alberta oil sands recovery. 25, 24, pp. 10 - 11.
- Oilweek (1975). Chemical cold water separation tested for oil sands. 26, 30, p.17.
- Oilweek (1975). New process noted for oil sands which would eliminate tailings ponds. 26, 36, pp. 14 - 17.
- Oilweek (1976). Costs, technology plague sands projects. 27, 35, p.10.
- Oilweek (1977). In situ oil sands project seen as possibility by 1980. 27, 48, p.9.
- van Olphen, H. (1963). Clay Colloid Chemistry, Interscience, New York.
- Oltmann, H.H. (1971). Beneficiation of phosphate rock. U.S. Patent 3,622,087, Nov. 23. To Dorr-Oliver Inc.

- Ottawa Report (1976). Syncrude saga continues; environmental responsibility still undefined, 1, 4, pp. 21 - 23.
- Oxford, T.P., and Bromwell, L.G. (1977). Planning for phosphate land reclamation. ASCE Specialty Conference, Geotechnical Practice for Disposal of Solid Waste Materials, Ann Arbor, June.
- Perkins, T.K. (1976). Production of bitumen from a tar sand formation. U.S. Patent 3,958,636, May 25.
To Atlantic Richfield Co.
- Petroleum Week (1960). Mining and ore disposal complicates sands development. Aug., pp. 20, 21.
- Puddington, I.E., and Farnand, J.R. (1968). Oil phase separation. Canadian Patent 787,898, June 18.
To National Research Council.
- Sparks, B.D., Meadus, F.W., and Puddington, I.E. (1971). The continuous separation of tar sands by oil-phase agglomeration. CIM Trans., 74, pp. 169 - 174.
- Meadus, F.W., Sparks, B.D., and Puddington, I.E. (1976). Apparatus for extracting at least one component from a material. Ger. Offen. 2,534,987, Mar. 11.
To Canadian Patents and Development Ltd.
- Rand, B., and Melton, I.E. (1975). Isoelectric point of the edge surface of kaolinite. Nature, 257, pp. 214, 215.
- Raymond, R.L., Hudson, J.D., and Jamison, V.W. (1970). Bacterial treatment of hot water process effluent discharge. U.S. Patent 3,502,566, Mar. 24.
To Great Canadian Oil Sands Ltd.
- Redford, D.A. (1976). In situ recovery from the Alberta Oil Sands. Chem. in Canada, Sept., pp. 20 - 23.
- Ribas, R.S., and Nickerson, J.D. (1976). Manufacture of phosphoric acid from phosphate matrix or tailings with minimized environmental effects. U.S. Patent 3,932,591, Jan. 13.
To United States Steel Corp.
- Ripley, M.J. (1972). The disposal of micaceous china clay waste in south-west England, in Tailings Disposal Today, Proc. 1st Int. Tailing Symp., Tucson, Ariz., Nov.
- Robinsky, E.I. (1975). Thickened discharge - a new approach to tailings disposal. CIM Bulletin, Dec., pp. 47 - 53.

- Rushing, J.C. (1973). Alumina plant tailings storage, AIME Annu. Meet., 102nd Proc. (Light Met. 1973). v.2, pp. 755 - 765.
- Schulz, K.F., and Morrison, D.N. (1973). Great Canadian Oil Sands tailings disposal problem, Parts I and II, Alberta Research Council.
- Schutte, R. (1974). Clarification of tar sands middlings water.
U.S. Patent 3,816,305, June 11.
To Gulf Oil Canada Ltd., et al.
- Schutte, R. (1975). Tailings disposal system for tar sands plant.
U.S. Patent 3,869,384, Mar. 4.
To Canada-Cities Service Ltd., et al.
- Scott, K.J. (1967). Significance of critical settling point in settling of flocculated slurries. Instn. Mining Metall. Trans. 76, c71 - c72.
- Scott, K.J. (1968). Theory of thickening. Factors affecting settling rate of solids in flocculated pulps. Instn. Mining Metall. Trans., 77, c85 - c97.
- Scott, K.J. (1970). Continuous thickening of flocculated suspensions. Ind. Eng. Chem. Fund., 9, P422.
- Sepulveda, J.E., et al (1976). Hot water extraction of bitumen from Utah tar sands. ACS - Div. Fuel Chemistry Preprints. 172nd Nat. Meeting San Francisco, 21, pp. 110 - 122.
- Shell Canada Ltd. (1975). Environmental impact assessment, lease 13 mining project, Alberta Oil Sands, 257 pp.
- Shewchuck, P.G. (1974). Alberta Oil Sands recovery plants water requirements and waste water management systems. Standards and Approvals Division, Environmental Protection Service, Department of the Environment.
- Shields, D.H. (1975). Innovations in tailings disposal. Can. Geotech. J., 12, pp. 320 - 325.
- Shirts, M.B., and Bilbrey, J.H. (1976). Stabilization methods for the reclamation of tailings ponds. Austral. Inst. of Min. and Metall., Adelaide Branch, Symp. Ser. n.13, pp. 9 - 18.
- Slobod, R.L., and Beiswanger, J.P.G. (1968). Use of polymers to control clay swelling. Petrol. Soc. of Can. Int. Mines, paper no. 6802.
- ✓Smiles, D.E. (1975). Some aspects of liquid movement in phosphate slime. Sep. Sci., 10, pp. 767 - 776.

- Somasundaran, P., Smith, E.L., and Harris, C.C. (1973). Effect of coarser particles on the settling characteristics of phosphatic slimes. Proc. 1st Int. Conf. in Part. Technol., Aug., pp. 144 - 150.
- Harris, C.C., Somasundaran, P., and Jensen, R.R. (1975). Sedimentation of compressible materials. Analysis of batch sedimentation curve. Powder Technol. 11, pp. 75 - 84.
- Specken, G.A. (1975). Clarification of wastewater from tar sands processing. Report on Alberta Environment Research Trust Project No. 95.
- Sprute, R.H., and Kelsh, D.J. (1976). Using slimes for backfill in deep mines. Min. Congr. J. 62, n4, Apr., pp. 22 - 26.
- Stanczyk, M.H., Field, I.L., and Collins, E.W. (1971). Dewatering Florida phosphate pebble rock slime by freezing techniques. U.S. Bureau of Mines, Rep. Invest. 7520, June, 20 pp.
- Stastny, G.J. (1973, 1974). Some methods for treating tar sands tailings, Report to Alberta Environment, Pts. I and II.
- Strosher, M.T., and Peake, E. (1976). The evaluation of wastewaters from an oil sand extraction plant. Report on EPS contract no. SS02-KE204-5-EP32, Environmental Sciences Centre (Kananaskis) University of Calgary.
- Stumm, W., and Morgan, J.J. (1972). Aquatic Chemistry. Wiley - Interscience, New York.
- Synchrude Canada Ltd. (1973). How will the Synchrude project affect the streams and lakes of the tar sands region? 5 pp.
- Synchrude Canada Ltd. (1974). How will Synchrude's mining activities affect the environment? 11 pp.
- Synchrude Canada Ltd. (1973). Environmental impact assessment, vols. 1 - 4. Sept.
- Terichow, O., and May, A. (1973). Electrophoresis and coagulation studies of some Florida phosphate slimes, U.S. Bureau Mines, Rep. Invest., R17816, 8 pp.
- Terichow, O., Sullivan, G.V., and Landis, E.K. (1975). Electrophoretic and filtration studies of a Florida phosphate slime. U.S. Bureau Mines, Rep. Invest., R18028, 17 pp.
- Theng, B.K.G., (1972). Formation, properties and practical application of clay-organic complexes. J. Royal Soc. New Zealand, 2, pp. 437 - 457.
- Thompson, J.L. (1973). Stabilization of water sensitive clays. U.S. Patent 3,738,425, June 12. To Dow Chemical Co.

- Tollefson, E.L. (1976). Third interim report to the Alberta Environmental Research Trust on the removal of hydrocarbons from aqueous waste water from oil sands recovery operations. Sept.
- United States Department of the Interior, Bureau of Mines (1975). The Florida Phosphate Slimes Problem. A Review and Bibliography, Inform. Circ. 8668, 41 pp.
- Vasan, S. (1972). Utilization of Florida phosphate slimes. Proc. Miner. Waste Util. Symp., 3rd, pp. 171 - 177.
- Vogt, M.F., and Stein, D.L. (1976). Dewatering large volume aqueous slurries; sand bed filtration of bauxite residue. Light Met., Proc. of Sess., AIME Annu. Meet., 105th, New York, v. 2, pp. 117 - 132.
- Walters, E.J. (1974). Review of the world's major oil sands deposits. Canadian Soc. Petrol. Geol. Conf. Proc., Sept., pp. 240 - 263.
- van Wazer, J.R. (1961). Phosphorus and its components, vols. I and II, Interscience, New York.
- Weir, S.R. (1972). Concentrating slimed minerals.
U.S. Patent 3,670,883.
To Engelhard Minerals and Chemicals Corp.
- Western Research and Development Ltd. (1976). Evolution of pollution abatement technology as applied to the Alberta Oil Sands. Report to Alberta Environment, March, 162 pp.
- Witt, E. (1972). Flocculation of particles dispersed in aqueous media.
Canadian Patent 909,981, Sept. 12.
To Standard Brands Chemical Industries Inc.
- Wright, H.J.L., and Kitchener, J. A. (1975). The problem of dewatering clay slurries: factors controlling filtrability. J. Colloid Interface Sci., 56, pp. 57 - 63.

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