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Potential Applications of Oil Sands Industry Wastes

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ABSTRACT

The processing of oil sands results in the production and storage of significant amounts of waste materials, including: large volumes of fine tailings from the separation of bitumen from oil sands and petroleum coke produced during the bitumen upgrading process. In several previous investigations we explored the production of potentially marketable products from these wastes. This paper is a review of work from the authors' laboratory. Several case studies illustrate the potential uses for coke and value,added products separated from fine tailings.

Delayed and fluid coke from bitumen upgrading are effective sorbents for both bitumen and naphtha. They are also excellent collectors for heavy metals. Based on these properties and a plentiful supply at relatively low cost, these materials provide an excellent medium for treating oil-in-water emulsions, for adsorbing oil spills, for heavy metal trapping in the purification of industrial effluents, for the treatment of oily waters, for extracting hydrocarbons from ground water and for the removal of odors.

Our work relating to the incorporation, or coating, of coke particles with lime or limestone is beneficial in the use of this material as an ancillary fuel with much reduced sulphur dioxide emissions. The ash from the combustion of coke can be leached to separate heavy metals. The leached residue could have potential applications as a flocculant for the treatment of fine tailings and possibly for the remediation of acid mine drainage.

The fine tailings are separable into several potentially valuable by-products such as: bitumen for production of synthetic crude oil or as an ancillary fuel, clean kaolin for fine paper coating, a gelling agent, emulsifying solids for surfactant replacement, and a mineral fraction rich in heavy metals.

INTRODUCTION

The production of refinery grade oil from the Alberta oil sands deposits as currently practiced by Syncrude and Suncor, generates a substantial amount of waste including, coke, fly ash, coarse sand and fine tailings. Under current production conditions, a plant producing 15,900m^3/day (100,000 bbl/day) of synthetic crude oil requires the processing of 100,000 m^3/day ore which results in a tailings stream consisting of 100,000 m^3 of coarse sand, 2,000 m^3 of coke, 100 m^3 of fly ash and 20,000 m^3 of Mature Fine Tailings (30% solids)[1-2]. As a result, a large inventory of process-affected materials are accumulating. The major concern regarding these wastes is a question of the volumes involved and the lack of an acceptable reclamation option.

The recognition and exploitation of the useful intrinsic properties of waste materials are becoming more important owing to increasing awareness of environmental issues. However, the commercial recycling of oil sands industry wastes has been limited to the use of sulphur and the burning of small amounts of coke. Recently, however, there has been extensive investigation of heavy metal recovery from centrifuge rejects and aluminum production from clay[3]. It is anticipated that high disposal costs and increased regulatory pressures to minimize landfill disposal options will increase the incentives for recycling by-products from these oil sands industry wastes.

For the past several years, we have been developing separation techniques for the recovery of by-products from oil sands industry wastes[4-10]. The principal objective of this work has been to develop technically feasible separation techniques for potentially marketable products. In these investigations we evaluated separation technologies in bench scale experiments using samples from both Suncor and Syncrude plants. Recently, we reported a preliminary evaluation of the technical and economic feasibility of utilizing oil sands fine tailings as a source of commercially marketable products after fractionation using NRC developed agglomeration-flotation technology[11].

This paper reviews our previous work to illustrate potential applications for coke, fly ash and by-products from fine tailings.

CASE STUDIES

1. Fine Tailings

Fine tailings are one of the undesirable end products of the hot water extraction processes currently used by Syncrude and Suncor. This fluid waste, which is currently stored in large tailings ponds on the Syncrude and Suncor sites, constitutes the largest and most difficult reclamation problem for the oil sands industry. At current mining levels, the equivalent of about 20 million m^3 of thickened fine tailings are added each year to the tailings ponds. The poor consolidation property of these fine tailings is responsible for the current practice of temporary storage in sedimentation basins until proper disposal options have been finalized.

The work carried out in our laboratories over the past several years has demonstrated that fine tailings can be separated into several potentially marketable components[11]. Included are: bitumen, for production of synthetic crude oil or ancillary fuel[5,6,8,12]; clean kaolin, for fine paper coating; a gelling agent, for drilling mud applications; emulsifying solids, for surfactant replacement and a mineral fraction, for the recovery of titanium and zirconium[7]. Based on a preliminary economic assessment of the worth of these components as basic raw materials the value of oil sands tailings has been estimated at $8-12/$m^3$[3].

Oil phase agglomeration or flotation is the basis of separation used in this work. This process, under development at the Institute for Chemical Process and Environmental Technology at NRC, relies on selective wettability between mixtures of liquids and solids of different hydrophobic or hydrophilic character to effect a separation of the components. Typically, a hydrophobic solid, such as ground coal or coke, is vigorously agitated with the fine tailings. During this process the residual oil content is selectively adsorbed by the coal or coke to form liquid films of oil on the particle surfaces. Continued agitation of the mixture brings the oiled adsorbent particles into repeated contact with each other, resulting in the formation of interparticle liquid pendular bonds. The end result is the formation of agglomerates comprising oil and adsorbent which may be separated from the aqueous phase by screens, cyclones or flotation [13-16]. These coal/coke-oil agglomerates can be used as an ancillary fuel after pelleting with limestone [8,9,12].

The process for the recovery of residual hydrocarbon from fine tailings by oil phase agglomeration is analogous to the process used previously at the National Research Council of Canada for the recovery of fine coal[17]. This work has encompassed process demonstration at the laboratory, pilot and commercial scale. Results from laboratory tests have been verified at both the pilot and commercial plant scale[18], demonstrating the feasibility of predicting full scale process behaviour from small scale trials.

The heavy metals in oil sands tend to be associated with a high concentration of strongly adsorbed organic matter in relatively large aggregates[19]. As a result of their high organic content these solids have hydrophobic surface characteristics and are usually closely associated with bitumen. Consequently, during bitumen separation by oil agglomeration, heavy metals report with the bitumen.

Once the bitumen and heavy metal components are removed, other useful materials may be separated using a series of centrifugation steps to fractionate the solids by particle size for specific applications. Figure 1 summarises the separation scheme. A final step involves emulsion flotation of the finest material to isolate Pickering solids (biwetted ultrafines) from the remaining hydrophilic ultra-fine fraction. About 30% of the fine tailings solids are recoverable as useful products. The remaining solids are relatively coarse and readily settle to a dense sediment. Concentration of the fines fractions by ultra-filtration, to reduce volume, results in the release of water for recycle to the primary bitumen extraction process.

The end uses for the products from fine tailings separation are predominantly in the petroleum or pulp and paper industries. Both of these business sectors are well established in Northern Alberta. Consequently transportation costs from Fort McMurray should not be an adverse factor. A 50 tph (dry solids basis) plant is within established design experience for an oil-agglomeration facility. Such a plant, operating 24 hours per day, year round, with an 80% on stream factor, would process about $1x10^6$ m^3 of fine tailings and produce approximately 100 kt/y of products, having a market value of \$8-12x10^6. A plant with this capacity would not have a significant effect on the accumulated volume of tailings at Syncrude but it could play an important role at the Suncor plant where the total amount of stored tailings is much less. In any case, this tailings treatment approach would require integration into the long term development plans for site remediation; it does not represent a short term solution.

2. Scroll Centrifuge Tailings

Scroll centrifuge tailings, produced at the dilution-centrifuge plant, during the treatment of bitumen froth for the removal of water and solids, are known to be enriched in titanium and zirconium minerals[20]. These tailings would provide sufficient feed for a large-scale titanium pigment plant, and sufficient zircon to satisfy Canadian demand for metallic zirconium[22]. As these minerals are preferentially wetted by bitumen[21] and are hydrophobic, this property may be used to beneficiate these minerals using the oil phase agglomeration process.

Several preliminary tests were carried out on a sample of Syncrude scroll centrifuge tailings to determine the viability of oil phase agglomeration to concentrate titanium and zirconium with ground Syncrude petroleum coke. The crude tailings contained 2.5w/w% bitumen and 19.3w/w% water with the balance being solids; approximately 20% of the solids were finer than 60 μm.

Figure 2 is a flow diagram for the agglomeration procedure. Non-optimized, small scale laboratory tests were used to produce a coke-oil-solids concentrate from ground coke and as received samples of scroll centrifuge tailings. These concentrates contained 25% TiO_2 and 1.8% ZrO_2 respectively. In these tests over 90% recovery of titanium and close to 100% recovery of zirconium was achieved.

Owing to the limited project budget, process optimization to determine the most favorable set of conditions for maximum titanium and zirconium recovery or grade, was not carried out. Also, scale-up information will require bench-size agglomeration tests.

The oil phase agglomeration process produces a heavy mineral feedstock best suited to the environmentally friendly chlorination process for TiO_2 manufacture[7]. This technology is preferred to the sulphuric acid process for the following reasons[20]: (a) low ratio of Fe to Ti; (b) ability to accommodate higher levels of impurities, such as Cr, (c) lower production costs; and (d) less waste disposal because chlorine can be recycled.

3. Sulphur

Sulphur produced as a by-product of the upgrading of bitumen to synthetic crude oil is already available for local use or for export. The largest use for sulphur is for the manufacture of sulphuric acid, much of which is further processed into fertilizers and a variety of chemical products

5. Coke

The coking processes used in the upgrading of Athabasca oil sands bitumen, to form a synthetic crude oil, produces approximately 4,000 m^3 of coke per day[2]. This coke is rather intractable as a fuel, being high in organic sulphur, low in volatiles, difficult to grind and containing relatively unreactive carbon forms[23-24]. Owing to serious environmental and corrosion problems associated with the combustion of this coke, its use as a boiler fuel has been limited and a significant portion of the coke is being stockpiled as a waste product.

In our laboratories we have used liquid-phase agglomeration techniques[5-6], with oil sands petroleum coke from both Suncor and Syncrude plants, to recover bitumen or heavy oil from waste water, produced in oil sands surface mining or in situ recovery operations. The addition of ground coke to the agitated waste water resulted in adsorption of the residual oil by the coke particles and the subsequent formation of coke-oil agglomerates. The agglomerates can be further treated to recover oil or they can be used as an enriched fuel source after pelleting with limestone.

The coke used to collect oil from aqueous effluents also acts as an adsorbent for dissolved organics. Tests on the aqueous phases for a number of systems have shown a reduction of total dissolved carbon from 300-600 ppm down to less than 50 ppm. According to EPA method 413.2 no oil or grease was present after this treatment.

Oil sands coke with a calorific value of about 33 MJ kg^{-1} would be an attractive boiler fuel if it could be desulphurized economically. Fluidized bed burners, incorporating limestone as a sulphur adsorbent, are emerging as a promising technology capable of high combustion efficiency and significantly reduced sulphur dioxide emissions[24-26]. However, it has been demonstrated that this approach ·equires relatively high calcium to sulphur mole ratios, even vith ash recycle, to produce acceptable sulphur dioxide :missions[27]. The development of combined fuel-sorbent ›ellets or briquettes for use as a sulphur dioxide control nethod has been reported to give superior sulphur dioxide mission control during combustion [28-29].

We have developed a novel technique whereby sulphur ioxide adsorbents can be incorporated directly into coal or oke agglomerates during liquid phase agglomeration using itumen or heavy oil as the binder[8,9,12]. This technique lows the advantageous use of very small and more active ılphur adsorbent particles in fluid bed combustion by nding them tightly within larger coke agglomerates, ereby reducing the possibility of their elutriation from the :d. As a result, higher adsorbent utilization efficiencies can obtained for the coagglomerated fuel, compared to those stems in which a coarser adsorbent is added separately to ɜ fluid bed.

Samples of petroleum coke from both Suncor and ncrude operations were successfully co-agglomerated with ıer limestone, lime or hydrated lime using bitumen as the ;ding liquid. When burnt at the optimum temperature ;50 °C), in a bench scale fluidized bed apparatus, this co- ;lomerated material emits significantly less sulphur oxides n comparable agglomerates without additives. Figure 3 ws the sulphur dioxide emissions as a function of Ca:S o in the co-agglomerated material[9]. Test results indicated)hur capture of over 60 wt.% for Syncrude coke and over wt% for Suncor coke at a calcium to sulphur molar ratio :1.

'igure 4 describes the comparative SO_2 capture :iencies for three sorbents. With the observed scatter of lts, no significant difference in sulphur capture between :hree additives was detected. However, the fact that the stone used in this series of tests gave results as good as or hydrated lime has considerable economic .ficance. The cost ratio of limestone, on a molar basis, vary from 2 to 4 times that for lime, depending on the portation distance. Even the costs for transportation and handling of limestone tend to be lower than for lime because limestone can be transported in open trucks. Also, limestone is readily available in the Athabasca region of Alberta.

The data in Figure 5 compares the levels of sulphur dioxide emissions, from both Syncrude and Suncor coke, with proposed US and Canadian emission standards. This figure clearly illustrates that a sulphur capture capacity of more than 80% may be needed to burn these cokes to meet SO_2 emission standards. Our test results suggest that co-agglomeration of finely divided sulphur dioxide sorbents in amounts representing a Ca:S molar ratio of 1 to 2 could result in the reduced SO_2 emissions necessary to achieve these emission levels.

Co-agglomeration of coke with calcium compounds will have the added advantage that the ash from the burnt agglomerates will be more suitable for the recovery of nickel and vanadium by acid leaching[30]. The ash residue from the burning of coke-oil-limestone agglomerates could also have potential applications as a flocculant for fine tailings and possibly for acid mine drainage treatment.

Based on its excellent adsorption potential oil sands coke also offers itself as an excellent medium for treating oil-in-water emulsions, for extraction of hydrocarbons from ground water contaminated by leakage of petroleum products from underground storage tanks, pipelines and other facilities. Other potential applications of oil sands petroleum coke include water treatment for the removal of odors, dissolved organic matter, oils, heavy metals and phosphorous.

5. Fly Ash

The fly ash, a by-product of burning coke produced from Athabasca oil sands bitumen, contains significant quantities of vanadium, titanium, nickel and iron[31]. It is a potential source for 2 million pounds annually of combined nickel and vanadium[32]. However, the metal values in this fly ash are not particularly amenable to acid leaching[33]. Preliminary tests in our laboratory have shown that oil phase agglomeration technology is particularly suitable for the beneficiation and eventual recovery of metals and carbon values from fly ash[34]. Incorporation of small amounts of limestone during beneficiation stages will possibly render the concentrate amenable to acid leaching.

CONCLUSION

This paper has shown that oil sands industry wastes can be exploited for the production of several potentially marketable byproducts. These include: residual bitumen, titanium dioxide, zircon and kaolin from fine tailings; titanium dioxide and zircon from scroll centrifuge tailings;

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enriched fuel with reduced sulphur dioxide and oil adsorbent from cokes and nickel and vanadium from coke fly ash. Market size analysis suggests a strong Canadian market for most of these byproducts.

Small scale tests carried out in our laboratory have demonstrated that the oil phase agglomeration process can be successfully applied for the production of these byproducts from oil sands wastes. Based on our extensive experience with oil agglomeration for the recovery of fine coal we suggest a 50 tph (dry solids basis) plant for the treatment of fine tailings. Such a plant would produce about 100kt of diversified products for the resource industry. Approximately 1×10^6 m^3 per year of tailings would be eliminated; an operation of this magnitude could be significant at the Suncor plant.

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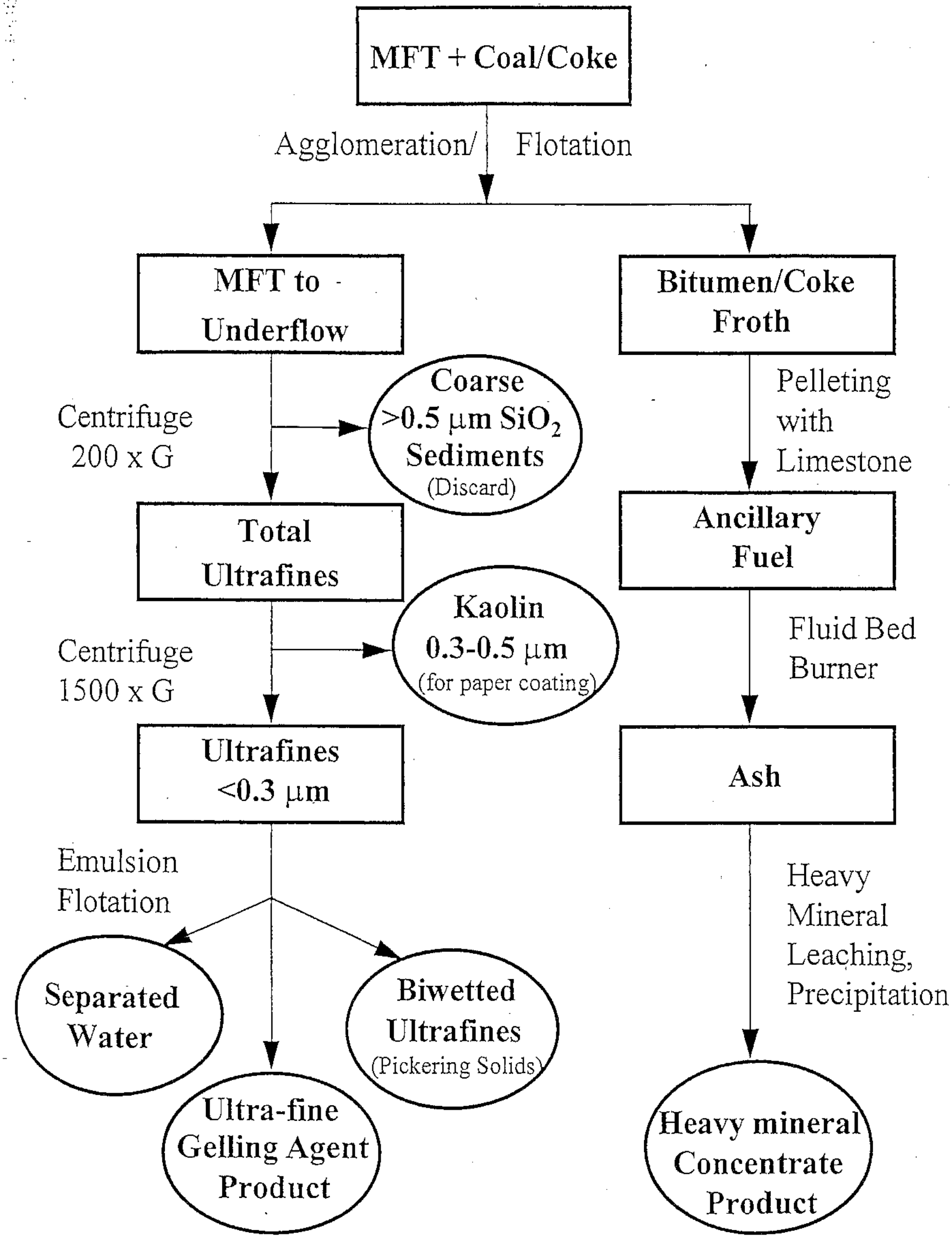

Figure 1. Overall Block Flow Diagram for Product Separation from MFT

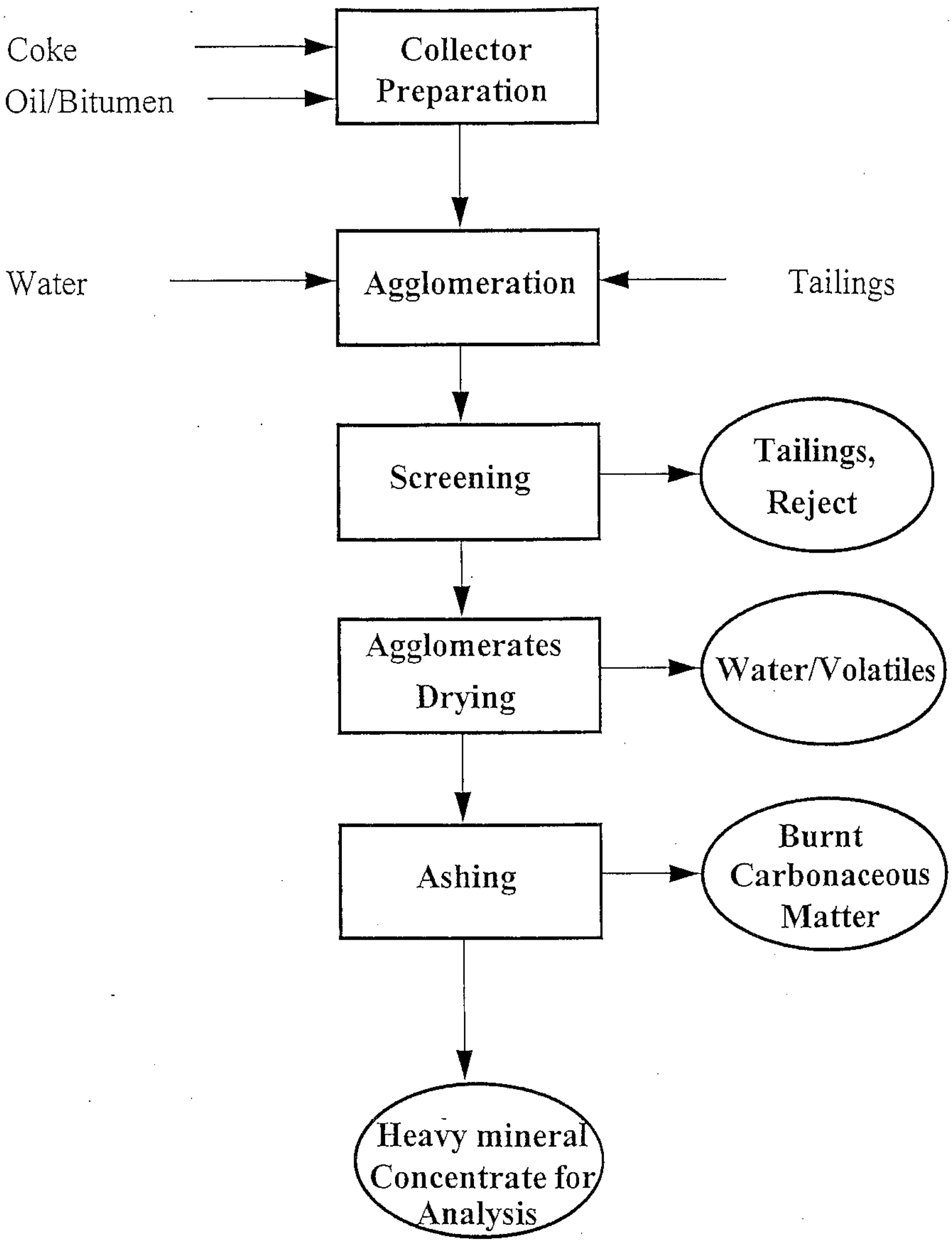

Figure 2. Agglomeration Test Flow-diagram

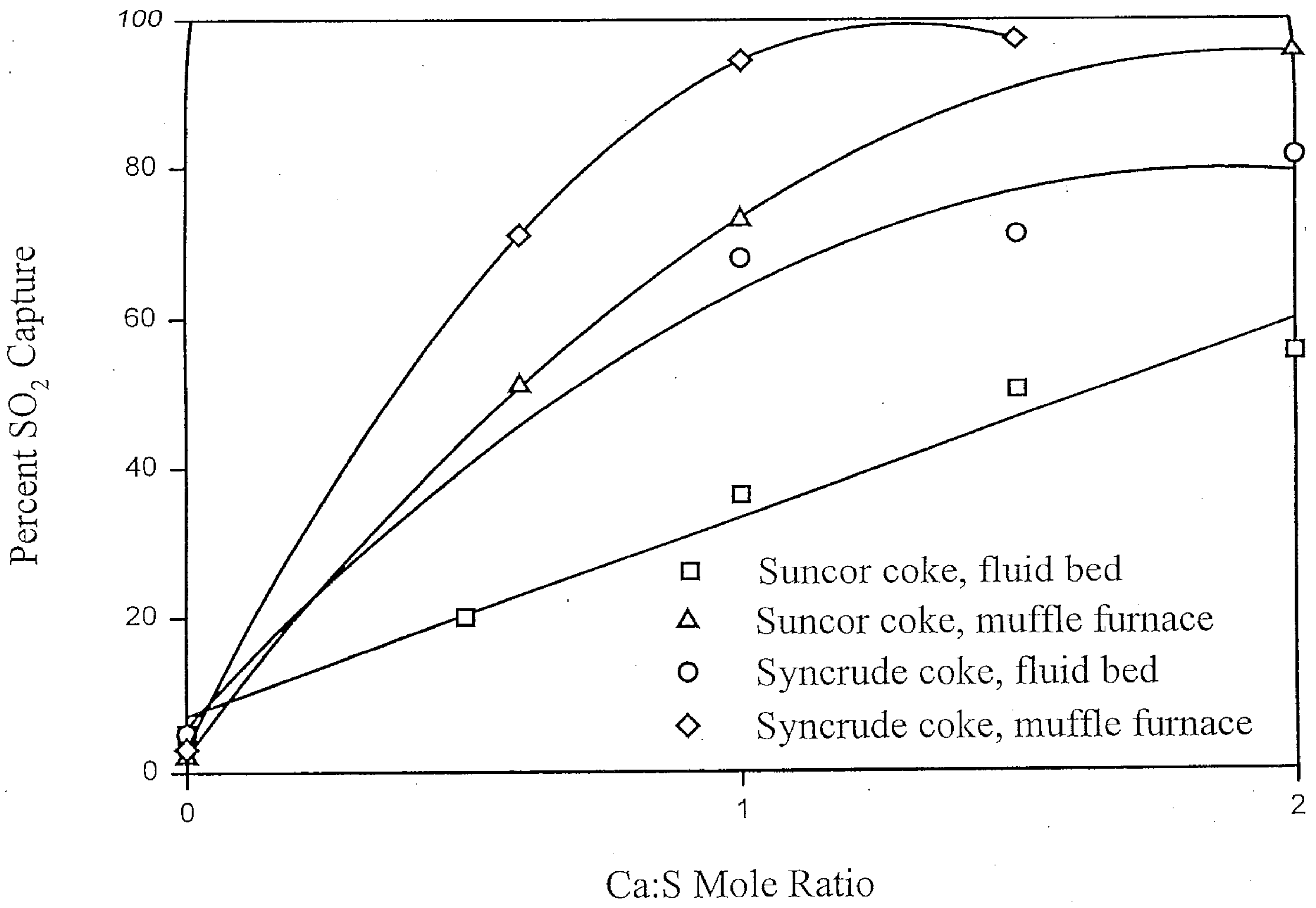

Figure 3. Effect of Ca:S molar ratio on the retention of SO_2 by lime

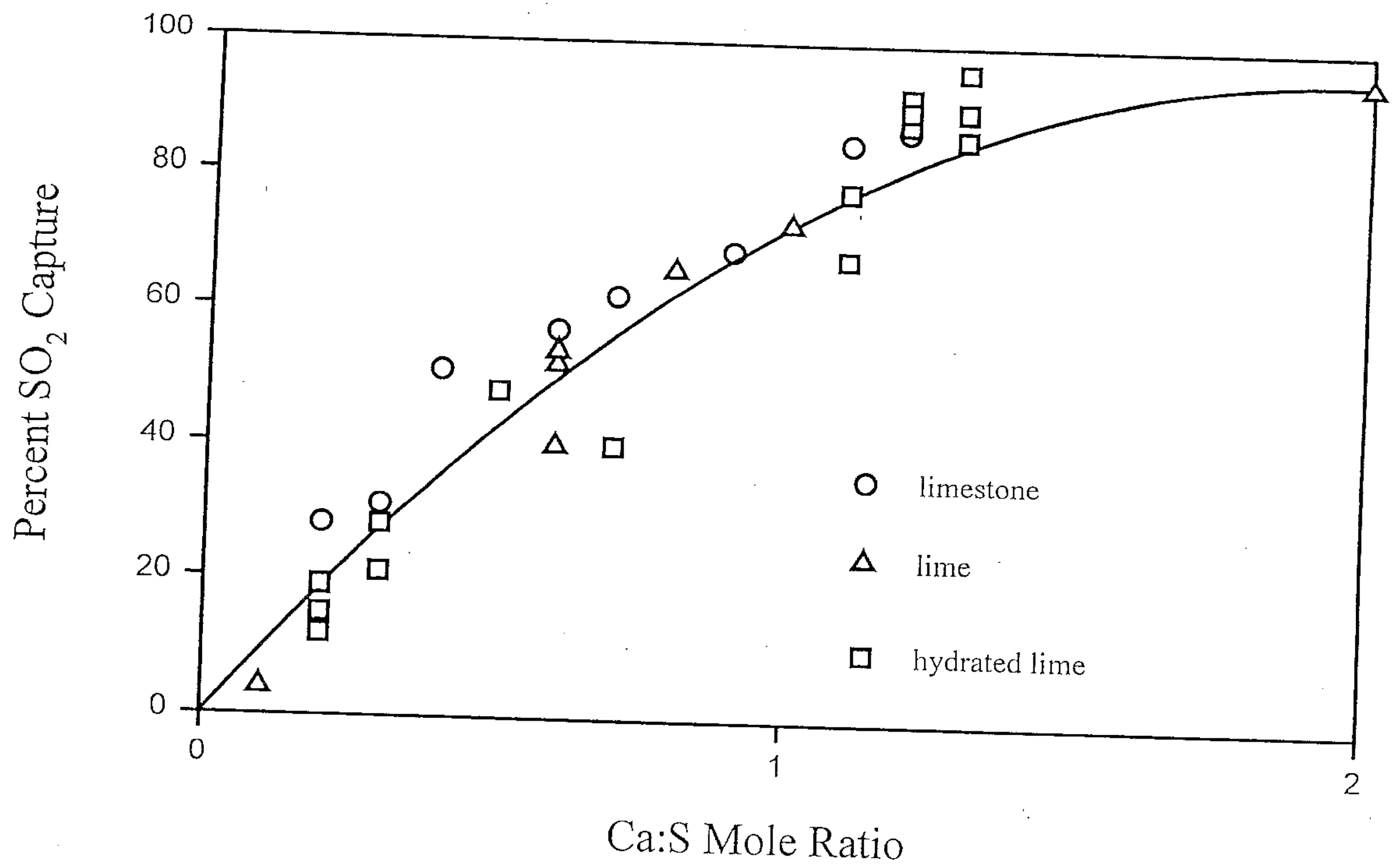

Figure 4. Comparative SO_2 capture efficiencies of various sorbents for Suncor coke

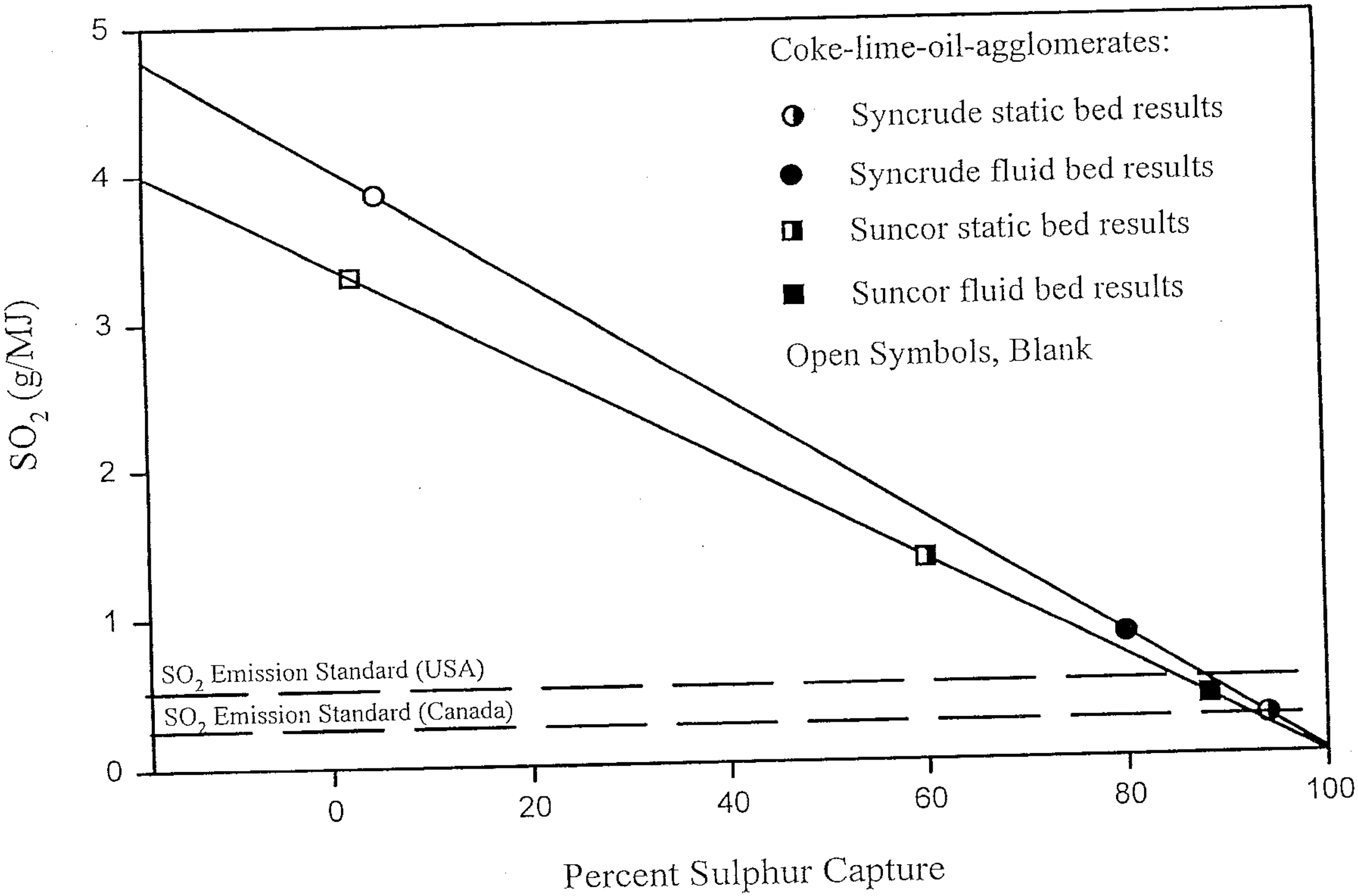

Figure 5 Levels of SO_2 Emission

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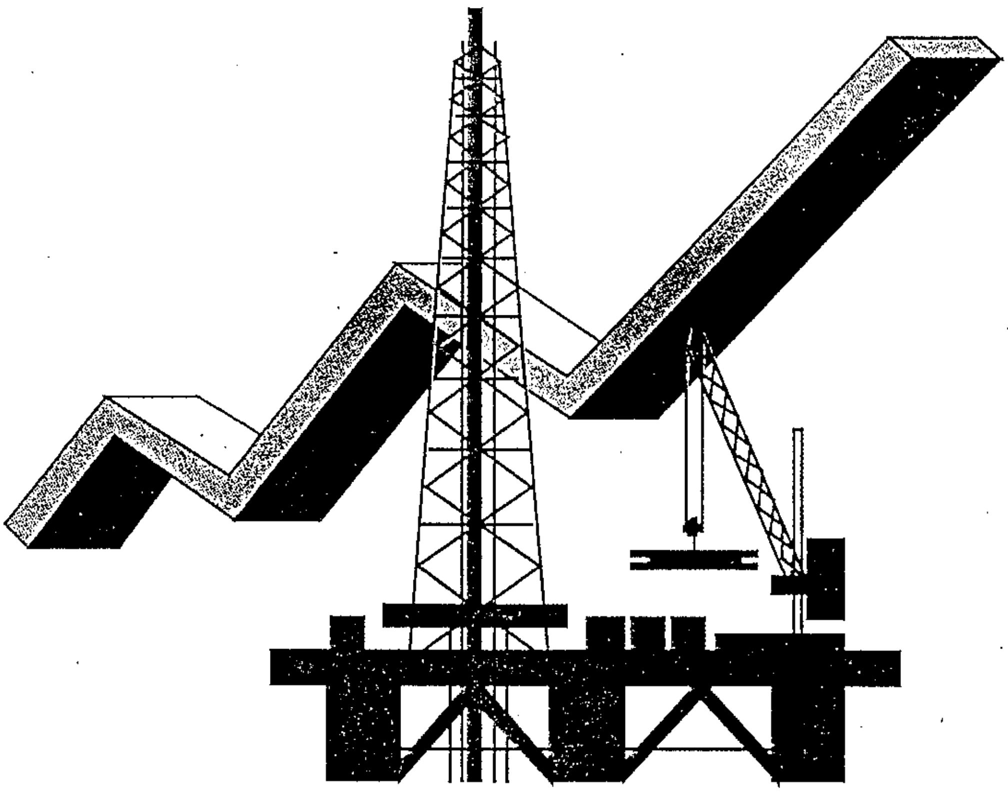

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