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coagglomeration of carbonaceous materials with sulfur sorbents**  
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stabilization of impurities to prevent leaching or to reduce emissions during combustion.

Liquid phase agglomeration (LPA) has the potential to play a major role in waste treatment processes (7-2). These range from the problem of waste tailings in the minerals and resource industries, to the disposal of organic sludges from petroleum production and refining operations to removal of sulphur impurities from coal or coke in order to mitigate the formation of acid rain. This process, under development at the National Research Council of Canada's Institute for Environmental Chemistry, relies on selective wettability, between mixtures of liquids and solids of different hydrophobic/hydrophilic character, to effect a separation of the components. Normally, a hydrophobic solid, such as ground coal or coke, is agitated vigorously with oil or oily sludge. During this process the oil is selectively adsorbed by the coal or coke to form a liquid film on the particle surfaces. Continued agitation of the mixture brings the oiled adsorbent particles into repeated contact with each other, resulting in flocculation of solids through the formation of interparticle liquid pendular bonds. These agglomerates, comprised of oil and hydrophobic carbon may then be separated from the aqueous phase using screens, cyclones or by degree of avidity for air bubble attachment, as in flotation. The type of separation scheme selected is governed by the degree of agglomeration achieved; this may range from weak floccules to densified, spherical agglomerates in which the voids are essentially saturated with oil. A more detailed description of the broad application of this process has been published in a number of review articles (3-5). Where water and hydrophilic solids are the contaminating phases in an oil based waste, then a hydrophilic solid adsorbent such as fine sand can be used as a collector for these components, leaving a clean oil (6). Similarly, emulsions can also be treated depending on whether they are water-in-oil or oil-in-water. It is usually more desirable to select an adsorbent which will preferentially collect the minor component in the material to be treated. A number of oily wastes have been effectively cleaned using solid carbonaceous materials for the recovery of residual oil (7-10). As well as collecting insoluble, oily contaminants a carbonaceous agglomerating solid may also adsorb most (80-90%) of the soluble organic species in a water based sludge. Consequently it is possible that such sludges can be cleaned effectively enough to allow direct sewerage of the treated water.

The cleaning of oily sludges by liquid phase agglomeration, using hydrophobic solid collectors such as ground coal or coke, has an added advantage in that not only is the oil adsorbed by the collector, but beneficiation of the collector, with respect to non-carbonaceous matter and pyrite also occurs during the process. However, organic sulphur will remain in the coal or coke matrix. This makes it imperative to include some form of desulphurization in any combustion system using this material as fuel.

The combustion of these agglomerates, with limestone addition, such as in a fluidized-bed reactor, could be one way to achieve the required reduction in sulphur dioxide emissions. However, it has been demonstrated (11) that this approach requires relatively high calcium to sulphur mole ratios, even with ash recycle, to produce acceptable reductions in sulphur dioxide emissions. Also, this technique precludes the use of finer sorbent particles that are known to be more efficiently

## Chapter 10

# Production of Low-SO<sub>2</sub>-Emitting, Carbon-Based Fuels by Coagglomeration of Carbonaceous Materials with Sulfur Sorbents

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A liquid phase agglomeration technique is being developed to incorporate sulphur sorbents into carbonaceous fuels. This paper reports a summary of the work describing a number of case studies, based mainly on the work from the authors' laboratory, to illustrate the diverse applications of the technique. Athabasca petroleum cokes obtained from Suncor delayed coking and Syncrude fluid coking operations and a high sulphur Nova Scotia coal were used for these tests. Static combustion tests at 850°C were carried out in a muffle furnace and compared with results found for a bench scale fluidized bed unit at the same temperature.

It has been demonstrated that greater utilization of the sulphur sorbent can be achieved by cogglomerating the fuel with sulphur sorbents, providing an environment in which there is intimate contact between fuel and sorbent compared with systems in which the sorbent is added separately to the combustion bed. Coagglomeration of petroleum cokes and lime (Ca:S molar ratio of 1:1), resulted in a percent sulphur capture of at least, 30% to over 80% depending upon the source of carbon and the test conditions (fluid bed vs muffle furnace).

Oily sludges and organic wastes are produced by a number of industries, particularly those related to the recovery and processing of petroleum. These wastes pose several challenges. Traditional sludge disposal methods, involving concentration by impoundment followed by land filling or land farming, are meeting with increasingly stringent regulations. Further treatment of the wastes and reduction of volume and recycle are being encouraged and legislated. Such treatment may range from separation of constituents into higher value products, such as the separation of oil or other organic components from mineral (ash forming) impurities and water, to

utilized for sulphur capture. A major problem with such fine particles is that they are easily entrained in exhaust gases and thereby removed from the system. Incorporation of the sorbent into a pellet overcomes the problem of elutriation loss and allows finely ground particles to be used. The present research was designed to determine the feasibility of introducing finely divided sulphur dioxide capture agents into high sulphur fuels so that they will be more uniformly distributed and intimately contacted with other components within the fuel-sorbent agglomerates. On combustion the sorbent is expected to be more effective compared to a system in which it is added separately. Athabasca petroleum cokes, obtained from Suncor delayed coking and Syncrude fluid coking operations and a high sulphur Nova Scotia coal were tested for this purpose. This paper summarizes the work carried out with these materials.

### 1. Oily Waste Treatment

**Recovery of Residual oil.** The Hot Water Process for the separation of bitumen, from surface mined Athabasca oil sands, generates large amounts of oil-contaminated sludge. This sludge does not consolidate beyond about 35 w/w% solids and must be stored behind man-made dykes. Substantial quantities of bitumen and naphtha are lost to the ponds. For example, at the Suncor plant, pond #1 has a bitumen and naphtha content such that 2000 m<sup>3</sup>/day could be extracted over a period of ten years. Consequently there is a strong economic as well as an environmental incentive to treat the sludge in these ponds.

Coking processes used in the upgrading of Athabasca oil sands bitumen, to form a synthetic crude oil, produce approximately 4000 tpd of coke. This coke is rather intractable as a fuel, being high in sulphur, low in volatiles, difficult to grind and having some relatively unreactive carbon forms, (12). Because of serious environmental and potential corrosion problems associated with the combustion of this coke, its use as a boiler fuel has been limited and a significant portion of the material is being stockpiled as a waste product. However, oil sands coke with a calorific value of about 33 MJ kg<sup>-1</sup> would be an attractive boiler fuel if it could be desulphurized economically. This waste material is also an ideal adsorbent for the selective collection of oil from the ponds. A series of small scale bench tests (9) have been carried out using a laboratory high speed blender. Four main process variables were initially selected: blending time (min), amount of coke (wt. % of sludge), coke particle size (100% passing a given size) and the amount of dilution water (mls.), added to allow the suspension to be mixed properly. Blending was continued until the selected mixing time was completed. The treated slurry was then dumped onto a 100 mesh screen and the larger coke agglomerates separated from the remainder of the solids. After washing the agglomerates were analyzed for all components.

Results from these tests demonstrated that the amount and particle size of the oil adsorbent were the most important factors in achieving high oil recovery. When recovery of the organics was plotted against total available hydrophobic surface (total weight of coke times specific area) it was found that all the data fell close to a common curve as shown in Figure 1. An initial rapid rise in recovery upon addition

of coke gradually tails off to a plateau, at about 85% oil collection, which represents the maximum attainable recovery under the given set of mixing conditions. In some cases, insufficient oil may be present to allow the formation of granules large enough to be separated by screening. In this situation bubble flotation is probably the best alternative for separation of the oil/coke flocs/agglomerates.

Removal of the oil component from the sludge usually results in more rapid and complete settling and compaction of the previously stable sludge. When this occurs it is possible to recycle a greater proportion of the pond water to the Hot Water Process. Consequently the tailings pond could be reduced in size.

**Coagglomeration of Sulphur Dioxide Sorbents.** The agglomerates obtained from the treatment of oily wastes by liquid phase agglomeration have potential use as an ancillary fuel. However, the heavy oils bitumens, petroleum cokes and coals, either present in the waste or added for treatment, are often high in sulphur. Thus, on combustion the emissions of sulphur dioxide may be above acceptable levels. The development of combined fuel-sorbent pellets or briquettes for use as a sulphur dioxide control method has been reported to give superior sulphur dioxide emission control during combustion, (13-14). It has already been demonstrated that the Athabasca oil sands bitumen; which is present in oil sands waste streams as a residual oil, is a good wetting agent for both the hydrophilic sulphur dioxide sorbent and hydrophobic coke. Consequently it is possible to incorporate sulphur dioxide adsorbents, such as finely divided limestone, into the agglomerates obtained during the treatment of oily sludge, (15-20). Syncrude refinery coke was used to collect over 90% of the residual bitumen from a sample of oil sands fine tailings (Suncor), according to the liquid phase agglomeration procedure reported previously (8). The discrete coke-oil agglomerates, of approximately 1 mm size, obtained from these tests, were then successfully coagglomerated with limestone corresponding to a Ca:S molar ratio of 1.2:1. This operation was made possible by the powerful collecting properties of bitumen and allowed the advantageous use of smaller and more active sulphur sorbent particles in fluid bed combustion, by binding them tightly within larger coal agglomerates. This approach reduces the possibility of elutriation of the SO<sub>2</sub> sorbent particles from the bed and, higher sorbent utilization efficiencies can be obtained for the coagglomerated fuel, compared to those systems in which coarser sorbent particles are added separately to the fluid bed. Combustion tests at 850°C in a bench scale fluidized bed reactor indicated over 90% sulphur capture (unpublished data) for these samples.

Similarly, it is possible to use a wet agglomeration process to produce a conglomerate of coke and sorbent; samples from both Suncor and Syncrude operations were successfully coagglomerated with either limestone, lime or hydrated lime using bitumen as the binding liquid. During combustion of the coke-bitumen-sorbent coagglomerates, sulphur dioxide capture was found to depend mainly on the calcium to sulphur mole ratio, the combustion temperature, and the type of coke. Moisture content of the agglomerates did not have any significant effect on sulphur capture. The combustion tests on coke-sorbent agglomerates were carried out in either a bench scale fluidized bed apparatus at 850°C or a muffle furnace at 460-1000°C. Figure 2 shows the sulphur dioxide emissions as a function of Ca:S ratio

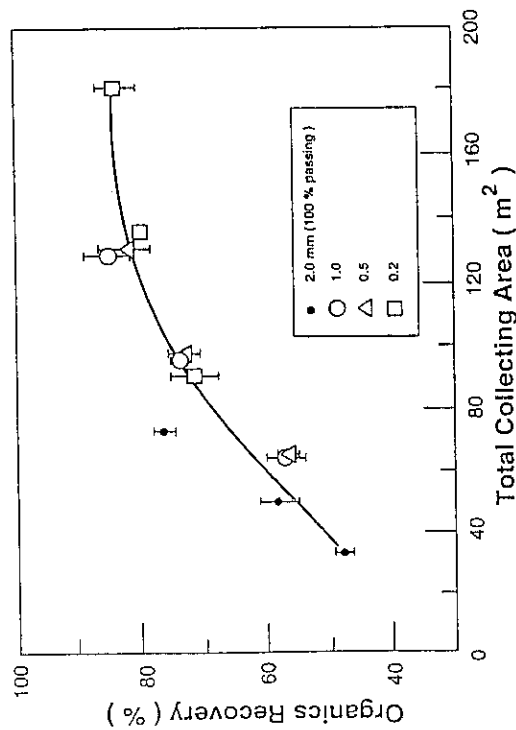
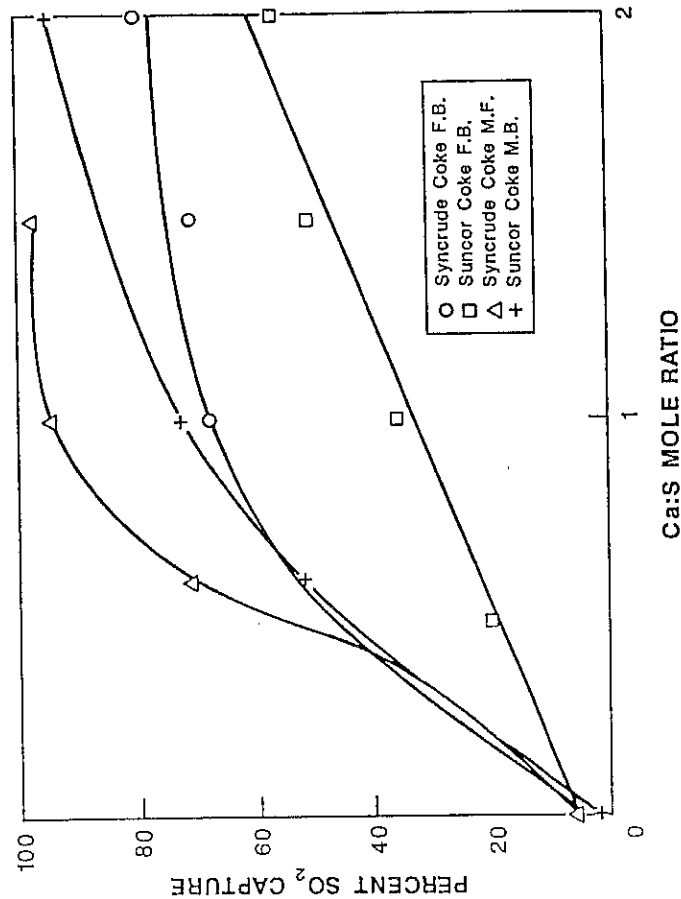


Figure 1. Oil recovery curve

Figure 2. Effect of Ca:S molar ratio on the retention of SO<sub>2</sub> by lime

in the coagglomerated material, (18). Test results indicated sulphur capture of over 60 wt % for Syncrude coke and over 30 wt % for Suncor coke at a calcium to sulphur molar ratio of 1:1. Figure 3 describes the comparative SO<sub>2</sub> capture efficiencies of the three sorbents. With the observed scatter of results, no significant difference in sulphur capture between the three sorbents could be detected. However, the fact that the limestone used in this series of tests gave results as good as lime or hydrated lime has considerable economic significance. The cost ratio of limestone on a molar basis may vary from 2 to 4, depending on the transportation 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.

According to the findings of Schneider and George (21), the presence of calcium also has a beneficial effect on the acid leaching of nickel and vanadium from coke ash. Hence, coagglomeration of coke with calcium compounds will have the added advantage that the ash from the burnt agglomerates will be more suitable for heavy-metal recovery as a byproduct of the combustion process.

## 2. Fine Coal Recovery

Agglomeration techniques have been used to recover coal from washery wastes and tailings ponds (1). Compared to flotation methods the process has been shown to be particularly effective for very fine materials. During recovery the coal is also beneficiated with respect to ash forming components and inorganic sulphur compounds, such as pyrites.

**Separation of Pyrite.** Two main problems are associated with the removal of pyritic sulphur from coals. The first is that pyrite is often in a fine state of dissemination, which requires grinding to a very fine size to accomplish liberation (22). The second problem is caused by the similar surface chemical characteristics of coal and pyrite, which complicates the use of separation methods based on surface wettability (23).

The problem of fine particle size for pyrite liberation can be partly overcome by the selective agglomeration method. With very fine grinding and the aid of a number of possible pyrite depressants under acidic, neutral and alkaline conditions it was possible (24) to remove 50% of the pyrite present in a high volatile bituminous coal. This agrees with the general difficulty experienced in removing pyrite by surface wetting differentiation as is used in both oil agglomeration and froth flotation. Recent work on coal beneficiation by liquid phase agglomeration has shown that aging of agglomerated coal could be advantageous in the beneficiation of pyritic sulphur (15). A sample of bituminous thermal coal from the Prince Mine, Cape Breton Island, Nova Scotia, was agglomerated with No. 4 fuel oil and stored in the laboratory for two months. This treated coal was then redispersed in water and reagglomerated with Athabasca oil sands bitumen; overall considerable further beneficiation with respect to non-carbonaceous matter and pyritic sulphur was achieved. In the second agglomeration step a reduction in pyritic sulphur of 80% was achieved compared to 40% in the original treatment. Ash content of the final

agglomerates was  $4\pm 0.1\%$  compared to 10.9% for the initial agglomerates and 19 % for the feed material. It is suspected that aging of the original coal agglomerates had resulted in selective oxidation of pyrite surfaces, thereby facilitating removal of this component because of the more hydrophilic nature of the oxidized particles. This is consistent with the successful removal of pyrite from coal using a combination of bacterial treatment followed by oil phase agglomeration, (25-26). Bacteria are known to oxidize pyrite, rendering the particle surfaces more hydrophilic; during this process surfactants are produced that could also affect the wettability of the components. However, coal surfaces, protected by an oil coating, are not significantly affected by either oxidation or surfactants.

**Coagglomeration with Sulphur Dioxide Sorbents.** Physical coal cleaning methods can remove only inorganic forms of sulphur, leaving the organic form in the coal matrix. Therefore, in addition to precombustion cleaning, inclusion of some form of desulphurization in any combustion system using this material as a fuel may also be necessary. Our earlier work on petroleum coke had demonstrated that coagglomeration of coke and sorbent as well as beneficiation, with respect to ash content of the coke can be achieved in a single step using a wet agglomeration process. Therefore, further work was carried out to determine the possibility of coagglomerating sulphur sorbents with coal as a means of reducing sulphur dioxide emissions during combustion. In a series of tests a run-of-mine sample of Nova Scotia coal was coagglomerated with limestone during the primary cleaning stage, using bitumen as binder. Static combustion tests at 850°C were carried out in a muffle furnace and compared with results found for a bench scale fluidized bed unit at the same temperature. The results are shown in Figure 4. In both cases, sulphur capture of over 60% was obtained at a calcium to sulphur molar ratio of 1:1.

Attempts to use LPA techniques to prepare a composite from the aged, agglomerated coal, limestone and bitumen were unsuccessful. It appears that the surfactants produced by pyrite consuming bacteria may prevent bonding of hydrophilic limestone with bitumen. Instead, the agglomerated, weathered coal was pelleted with varying proportions of limestone using a die and press. Combustion tests on these pellets were carried out in a muffle furnace at 850°C. The results, shown in Figure 5, also contain data for the run-of-mine coal/limestone agglomerates. This plot indicates similar sulphur retention results for the two types of agglomerates, suggesting that they both withstood the combustion conditions equally well.

#### Comparative Sulphur Capture Efficiencies

The data for cokes and coal has been combined in Figure 6 for comparison purposes. This is a plot showing the levels of  $\text{SO}_2$  emissions obtained for both blank and lime containing agglomerates of Prince coal, Suncor and Syncrude cokes. USA and Canadian  $\text{SO}_2$  emission standards are also shown on this plot. This Figure clearly illustrates that a Sulphur capture capacity of more than 80% may be needed to burn these fuels to meet  $\text{SO}_2$  emission standards. The data for coal/coke lime agglomerates plotted in the Figure shows that coagglomeration of fine sulphur

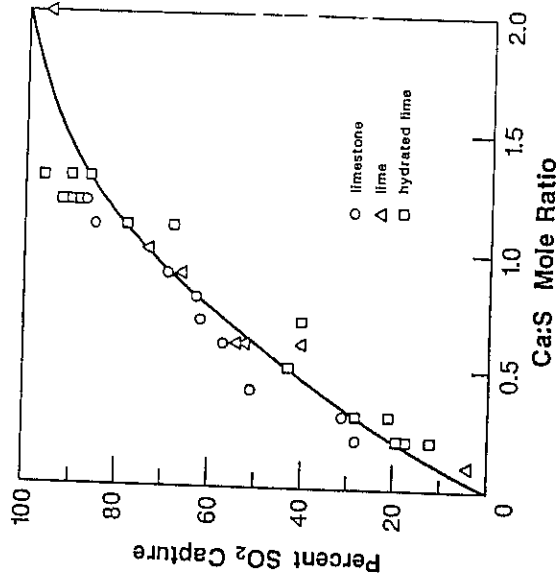


Figure 3. Comparative  $\text{SO}_2$  capture efficiencies of various sorbents for Suncor coke

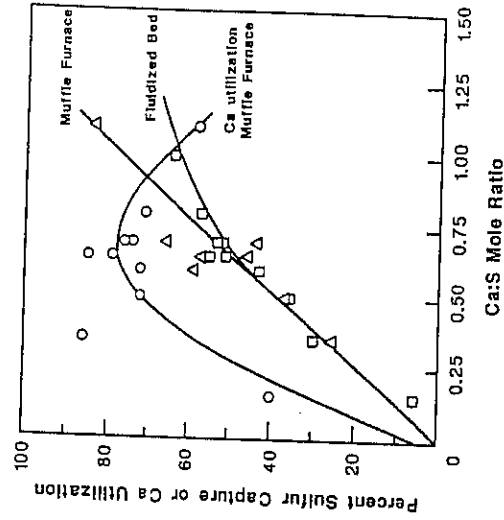


Figure 4. Effect of Ca:S molar ratio on sulphur capture and on Ca utilization

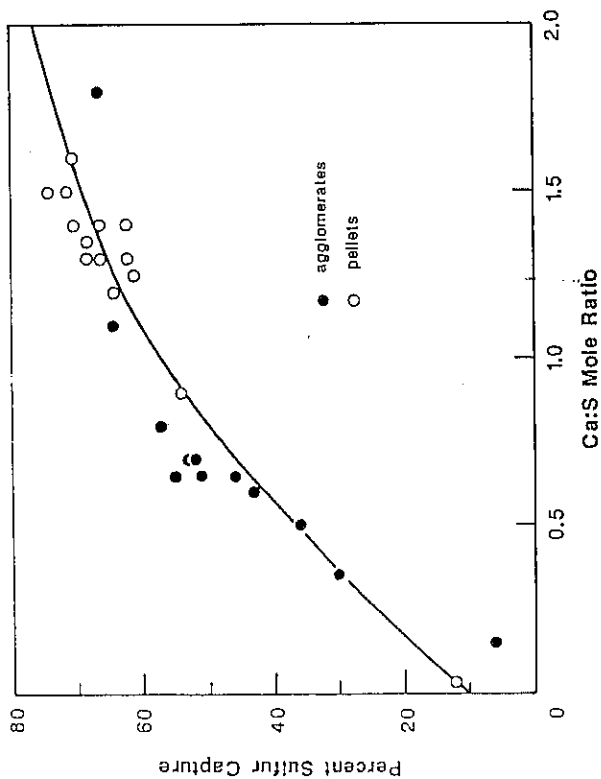


Figure 5. Effect of Ca:S molar ratio on sulphur capture for coal/limestone agglomerates/compacts during combustion in a muffle furnace

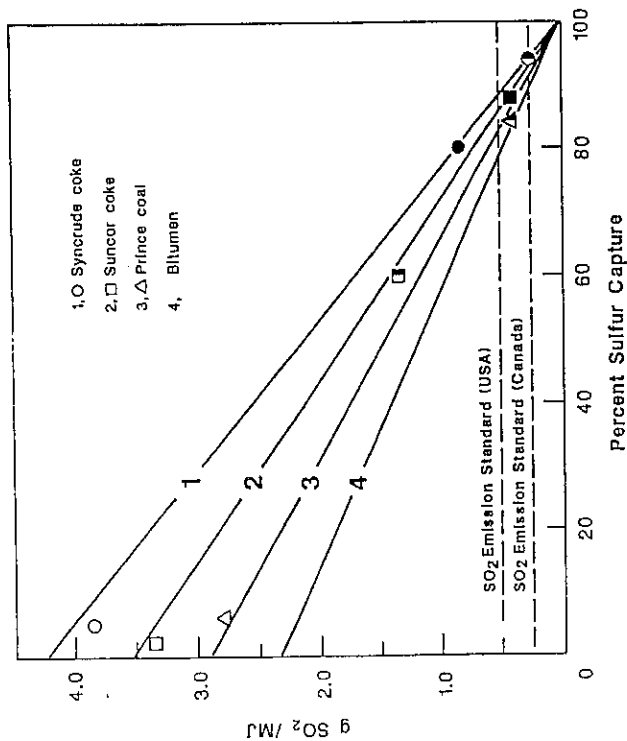


Figure 6. Levels of SO<sub>2</sub> emission; fuel-lime agglomerates (half closed symbols, static bed results, closed symbols, FBC). Ca:S molar ratios: coke 2, coal 1.1

sorbents in amounts representing a Ca:S molar ratio in the range of 1 to 2 could result in the reduced SO<sub>2</sub> emissions necessary to meet proposed standards.

### Conclusion

A liquid phase agglomeration process has been developed to incorporate finely divided sulphur dioxide capture agents into a variety of carbonaceous fuels. The resulting agglomerates had improved combustion characteristics and lower sulphur dioxide emissions compared with those for the original fuels. The decrease in sulphur dioxide emitted on combustion was found to depend on the calcium to sulphur mole ratio, source of fuel, and conditions of testing. The coal/coke-bitumen-limestone coagglomeration results suggest that coagglomeration of fine sulphur dioxide sorbents in amounts representing a Ca:S molar ratio in the range of 1 to 2 could result in the reduced SO<sub>2</sub> emissions necessary to meet USA as well as Canadian proposed emission standards. This chapter was issued as NRCC No. 35767.

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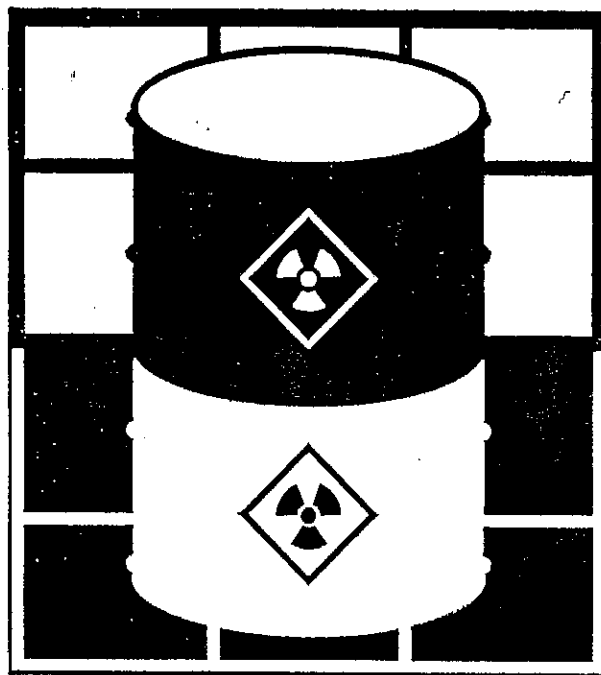
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