EVALUATION OF SO$_2$ SORBENT UTILIZATION IN FLUIDIZED BEDS

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December 1986

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Abstract

A bench-scale fluidized-bed reactor was used to evaluate more than forty lime-stone and dolomite samples from twenty-five deposits and quarries in Nova Scotia, New Brunswick, and Alberta for their ability to capture SO$_2$ emitted during the fluidized-bed combustion of coal. Nineteen of the samples were also evaluated by thermogravimetric analysis; a comparison of the two methods is given.

The detrimental effect of coal ash on the sulphation capacities of two lime-stones was studied. Sulphation appears to decrease with increasing iron oxide content in the ash.

Various methods of improving the limestone utilization in fluidized beds were investigated. Finely ground and pelletized limestone improved the sulphation capacity as much as five times that of the coarse limestone. Similar improvements were observed by hydrating partially sulphated bed material, and also by grinding and pelletizing used bed material.

The parameters of the sulphation curve equation derived from the FBR tests are incorporated with the operating data for large-scale fluidized-bed units in the Argonne National Laboratory model to predict the performance of the sorbents in those units. The model prediction compares very well with actual data from a pilot-scale fluidized-bed and the Summerside fluidized-bed combustor.

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ÉVALUATION DES PRODUITS DE SORPTION DU SO$_2$ LORS DE LA COMBUSTION EN LIT FLUIDISÉ

C.A. Hamer*

Résumé

Un réacteur à lit fluidisé à échelle-pilote a été utilisé pour évaluer plus de quarante échantillons de calcaire et de dolomite provenant de vingt-cinq gisements et carrières de la Nouvelle-Écosse, du Nouveau-Brunswick et de l'Alberta. Cette évaluation avait pour objet de déterminer la capacité de ces échantillons de capturer les émissions de SO$_2$ durant la combustion en lit fluidisé du charbon. On a employé l'analyse thermogravimétrique pour étudier dix-neuf échantillons; une comparaison de deux méthodes d'évaluation est aussi présentée dans le rapport.

Les effets nuisibles des cendres du charbon sur la capacité de sulfatation de deux échantillons de calcaire ont été étudiés. La réaction de sulfatation semble diminuer avec une augmentation de la teneur en oxyde de fer dans la cendre.

Diverses méthodes permettant d'améliorer l'utilisation des calcaires dans les lits fluidisés ont été étudiés. La capacité de sulfatation du calcaire finement broyé et granulé a augmenté plus de cinq fois par rapport à celle du calcaire grossier.

Des résultats semblables ont été observés en hydratant un produit partiellement sulfaté dans le lit, et en broyant et transformant en granules le produit déjà utilisé en lit fluidisé.

Les paramètres de l'équation de la courbe de la réaction de sulfatation, tirés des résultats d'essai avec le RLF ont été ajoutés aux données de fonctionnement des installations à lit fluidisé grandeur réelle du modèle informatisé élaboré par l'Argonne National Library, qui prévoit le rendement des sorbants dans des chambres à combustion grandeur réelle. La prédiction obtenue à l'aide du modèle se compare très bien aux données actuelles obtenues du lit fluidisé à échelle-pilote et de la chambre à combustion du lit fluidisé de Summerside.

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INTRODUCTION

The use of a limestone or dolomite to absorb and retain SO_2 is standard practice in the fluidized-bed combustion of coal. At the combustion temperature of 800-900°C, $CaCO_3$ decomposes to CaO and CO_2; the CaO then reacts with SO_2 and O_2 or SO_3 to form $CaSO_4$. Theoretically, one mole of calcium is required for each mole of sulphur released during the combustion of coal. In practice, however, a threefold or greater excess of calcium oxide is often required to capture 90% of the sulphur dioxide emitted. Thus, in an atmospheric fluidized-bed combustor (AFBC) burning 5% sulphur coal, limestone requirements of 0.5 kg/kg coal or greater would be common.

It has been well recognized that limestones and dolomites from different sources vary considerably in their ability to capture SO_2. The various physical and chemical parameters of carbonate rocks have been the subject of many investigations to determine the factors that affect the sulphur capture efficiency (1-6). These investigations have shown that the porosity of the calcined rock and the calcium content are major factors affecting performance as a sorbent. Although these data are indicative, they are inadequate to predict sorbent behaviour. Limestones and dolomites must be actually exposed to SO_2 containing flue gas at fluidized-bed combustor operating temperatures in order to determine their performance. This may be accomplished in full-scale or pilot-scale fluidized-bed units. However, if a number of potential sorbents are to be tested, the material and manpower requirements can be considerable. A more practical approach to evaluating or ranking a series of sorbents is to use thermogravimetric analysis (TGA) or a bench-scale fluidized-bed reactor (FBR). The use of models such as those devised by Westinghouse, Argonne National Laboratory (ANL), and others, which incorporate TGA or FBR data to predict sorbent performance in AFBC, makes these evaluation techniques particularly useful (7,8).

The Canada Centre for Mineral and Energy Technology (CANMET), a branch of Energy, Mines and Resources Canada, has been actively promoting AFBC technology as an environmentally acceptable method for combusting high-sulphur and low-grade fuels. An atmospheric fluidized-bed heating plant with two 18 Mg/h steam boilers was designed by Foster Wheeler Corporation and built in 1982 in association with the Department of National Defence at Canadian Forces Base Summerside (9). A one square metre AFBC, built in conjunction with Combustion Engineering Superheater Ltd., Canada and the Nova Scotia Power Commission, completed in July 1985 a 10 000 h corrosion test program to obtain information for future AFBC units (10). A 22 MW(e) circulating fluidized bed is being built by Combustion Engineering using Lurgi technology for the New Brunswick Power Commission and is scheduled for commissioning in late 1986 (11).

In addition to supporting large-scale units, CANMET operates pilot and bench-scale fluidized-bed units at the Combustion and Carbonization Research Laboratory (CCRL) (12) and at the Mineral Sciences Laboratories (MSL) (13). It also sponsors contract research in FBC technology at Queen's University and other research establishments.

An element in CANMET's fluidized-bed program being conducted in MSL is an investigation of Canadian limestones and dolomites as SO_2 sorbents. More than forty samples representing twenty-five deposits and quarries in Nova Scotia, New Brunswick, and Alberta were evaluated in a bench-scale fluidized-bed reactor. The first two provinces mine high-sulphur coal while the latter produces high-sulphur, unreactive coke from tar sands operations, all of which are potential fuels for FBC. Additionally, eight carbonate rocks from Sweden were tested. Nineteen of the Canadian samples were also evaluated by TGA. The data from these tests were applied to the ANL model to predict the performance of these sorbents in an AFBC similar to the Summerside unit. The performance predictions, combined with costs, can be used to determine the most effective limestone for use in present and future FBC units.

In AFBC the limestone particle size is range 3-0.5 mm, and in this size range the degree of conversion of calcium oxide to the sulphate is usually 15-45%, the mid-twenties being common. Thus, about 75% of the calcium content in the limestone is not utilized in the AFBC. Techniques to improve the utilization of sorbents were examined. Much of the study was on the use of finely ground limestone agglomerated as pellets. Also investigated was the effect of the coal ash on the sulphation capacity of sorbents.

LIMESTONE AND DOLOMITE

Sorbent Characteristics

In fluidized-bed combustion the common sorbent for SO_2 is CaO, which is introduced to the combustor as limestone, $CaCO_3$, or dolomite, $CaMg(CO_3)_2$. At the 800-900°C operating temperature range the rocks calcine to release CO_2, but only the CaO reacts with SO_2 and O_2 to form $CaSO_4$. $MgSO_4$ can form from the $MgO-O_2-SO_2$ reaction at lower temperatures, i.e., 650-750°C, but has a high equilibrium SO_2 concentration above 775°C and therefore does not capture significant quantities of SO_2 under AFBC operating conditions (14). It may capture some SO_2 in the flue gas downstream of the combustion chamber where the gas temperature decreases through the cyclones and heat exchanger. MgO from dolomite does capture SO_2 in pressurized fluidized beds (PFBC) that operate at 10 atm, but sorbent use in PFBC is not included in this study.

Limestones are sedimentary and metamorphosed sedimentary rocks formed mainly through the deposition of calcarious material on ancient sea bottoms or in depositional basins. They can vary from soft chalk and marl to crystalline marble, and form a variety of other minerals depending upon the composition of the original calcareous material, the conditions of metamorphism, and the elements added from adjacent rock masses or igneous sources.

Harvey and Steinmetz (3) investigated the influence of the petrographic properties of carbonate rocks on the sorption of SO_2. They found that the SO_2 capacity tended to increase with increasing pore volume and decreasing grain size of the rock. Potter (5) also found that pore size was more important than chemical composition in determining sulphation capacity. Both investigations were performed in fixed-bed reactors at 980°C, a higher temperature than normally encountered in AFBC systems. Munzer and Bonn (4) compared a number

of European limestones in a 60 mm diameter fluidized-bed combustor and con-
cluded that next to purity, i.e., the calcium content, porosity is the most
important parameter influencing sulphur capture. They found that on a Ca/S
basis, dolomites are usually more effective than limestones as sorbents.
Potter's results indicated that chalks had the best reactivity followed by
oolite, dolomite, and calcite in that order. Both Borgwardt and Harvey (6),
and Spitsbergen et al. (15), found that marls were the most reactive material
for SO_2 capture. As a general rule-of-thumb, the younger the geological age
of the rock, the greater its porosity and sulphur capture capacity.

The pore size and volume, combined with particle size, are the most outstand-
ing determinants of sorbent activity (1). In the reaction of SO_2 with CaO,
the product $CaSO_4$ forms on the surface and in the pores of the calcined lime-
stone. Because the molar volume of $CaSO_4$ (52.2 cm^3/g mol) is greater than
that of CaO (16.9 cm^3/g mol) or of $CaCO_3$ (39.9 cm^3/g mol), the reaction
product essentially seals the surface and the fine pores, retarding further
reaction of SO_2 with the unreacted lime core. In a dolomite, the $MgCO_3$ cal-
cines to MgO but does not sulphate, thus resulting in a more open structure
that allows more complete sulphation of the calcium oxide. A limestone with
a large pore volume made up principally of pores whose diameter is in the
order of 0.08 μm or greater after calcining, has a much greater SO_2 capacity
than a stone with a small pore volume composed of narrow mouth pores (2,16).
Small pores may facilitate high initial reaction rates, but they plug rapidly
and give overall low capacities. Large pore rocks may sulphate at a slower
initial rate but give greater overall capacity. Obviously, the smaller the
particle size, the greater is the surface area and exposed pore volume, and
the more complete is the limestone utilization. It is the pore size of the
calcined rock which is important rather than that of the raw limestone.

The chemical composition of limestone is principally calcium carbonate. Mag-
nesium is a common constituent that substitutes for calcium as a result of
transformation of limestones by magnesium-bearing solutions. The amount of
substitution can vary from practically zero to the composition of dolomite.
Some small fraction of the calcium and magnesium may be bonded as silicate
minerals and thus not be available to react with SO_2. Impurities of alumi-
num, silicon, and iron may be associated with the limestone as oxides and as
clays, quartz, siderite, and other minerals. Additionally, there will be a
host of trace elements.

Harvey and Steinmetz reported higher sulphation capacities with higher sodium
content in the sorbent (3). Sodium, if it is in a mobile species, can cause
a more porous calcine, as will be discussed later. Iron as Fe_2O_3 or FeO(OH)
also has been credited with a slight increase in reactivity (4,5). As pyrite,
however, iron reduces reactivity. Other impurities appear to exercise little
influence on sulphation.

Since only the CaO reacts with SO_2, obviously the higher the content of that
compound the higher will be the SO_2 capture capacity of the rock, providing it
has a porous structure to allow access of the SO_2 to the calcium. However,
the proviso of a porous structure is more important than chemical purity.
Greek marble, although more than 99% $CaCO_3$, is not porous and has a low SO_2
capacity.

Limestone Samples

The limestone and dolomite samples examined in this project have come from a variety of sources and agencies over the last five years. The initial samples were collected in 1981 and the remainder over the subsequent years. The complete list of samples and their source is given in Table 1. The quantity of sample received for each deposit or quarry was 10-40 kg. In the case of an undeveloped deposit, the samples were rocks from the surface or cuttings and drill cores for two Glencoe samples. The quarry samples were run-of-mine. The sample from Gays River, Nova Scotia, is a dolomite tailings from a lead-zinc mine and was included to determine whether this material could be pelletized and used as a sorbent. Unfortunately, the mine has since closed.

In September 1982, the author collected a number of samples at the Havelock Lime Works, Havelock, N.B. This company supplies limestone for the fluidized-bed unit at CFB Summerside. The company obtains its limestone from two quarries; their own at Samphill and also from Canada Cement Lafarge's at Havelock. Both quarries are in the same geological formation although about 9 km apart. Samples were taken from various locations in the quarry operations. Additionally, samples were available from several shipments since 1980 to CCRL and from shipments to CFB Summerside in 1982. Limestone from a bag of Havelock "Shell Mix" is used as the internal standard limestone. Two more samples from both quarries were received in 1986. Thus, 12 samples representing the production of one limestone plant operating on two quarries over a five-year period were available for testing.

Samples were reduced in size through a series of jaw and cone crushers followed by a disc pulverizer. Representative samples were taken for chemical analyses, the results of which are given in Table 2. Complete analyses were done on the initial series of samples, but only calcium carbonate content on the later samples. At the request of the Nova Scotia Power Corporation, the initial series of Nova Scotia samples were analyzed for as many trace elements as possible by spectroscopy. These results are given in Table 3.

Petrographic Studies

Three samples of limestone were examined in thin section to determine their physical characteristics. A detailed study of all samples was beyond the scope of this work. Photomicrographs of the three limestones, Irish Cove (NS-1), Calpo (NS-5), and Glencoe (NS-12) are given as Figures 1, 2, and 3. The calcium carbonate has been stained with alizarin red 5 dye to differentiate it from dolomite.

Irish Cove limestone is a fine-grained fossiliferous calcite in which occasional particles show grains of dolomite. Calpo is a fine-grained fossiliferous calcite in which most particles exhibit macroporosity. The Glencoe sample shows variable grain size up to fairly massive crystals that are recrystallized and interspersed with dolomite. Some particles are black and contain visible pyrite crystals. X-ray diffraction of the black particles indicated the presence of chlorite, pyrite, quartz, and mica. Therefore, although in the chemical analysis the magnesium is expressed as carbonate, some is actually magnesia silicate hydrate.

Table 1 - Source of limestone and dolomite samples

Nova Scotia

Samples NS-1 to 12, and GR-1, were collected by J. Fowler,
Nova Scotia Dept. of Mines and Energy

GR-1   Canada Wide Mines Ltd., Gays River, Halifax County.
        Sample of dolomite fines from the mine tailings pond,
        1981.

NS-1   Limestone from the Scotia Limestone quarry at
        Irish Cove, Cape Breton County, 1981.

NS-9   As above, 1982.

NS-2   Dolomite from the Scotia Limestone deposit at
        Kelly Cove, Victoria County, 1981.

NS-3   Dolomite from Mosher Limestone Co. Ltd., quarry
        Upper Musquodobit, Halifax County, 1981.

NS-13   Limestone from Mosher Limestone Co. Ltd., 1983.
        Submitted by Mosher Limestone.

NS-4   Limestone from the Canada Cement Lafarge Co. Ltd.,
NS-8   quarry at Brookfield, Colchester County, 1981.

NS-5   Limestone from Havelock Lime Works quarry at Southside
        Antigonish Harbour, Antigonish County. Also known as
        Calpo limestone, 1981.

NS-10   As above, 1982.

NS-6   Limestone from the Scotia Limestone deposit at Glenco,
NS-7   Inverness County, 1981.
NS-11   Composite sample from the 31 ft - 290 ft section of
        drill core D-8, Glencoe deposit, 1976-1977 (23).

NS-12   Composite sample from the 9 ft - 230 ft section of drill core J-2,
        Glencoe deposit, 1976-1977.

NS-14   Limestone from Glendale deposit, Inverness County. Supplied by
        W. Shaw, 1986.

NS-15   Limestone from East Bay deposit, Glen Morrison, Cape
NS-16   Breton County. Supplied by W. Shaw, 1986.

NS-17   Limestone from Gabarus Lake deposit, Cape Breton
        County. Supplied by W. Shaw, 1986.

NS-18   Limestone from Cape Dauphin deposit, Victoria County.
NS-19   Supplied by W. Shaw, 1987.

New Brunswick

Samples NB-2 to 5 were collected by D.E. Barnett,
New Brunswick Dept. of Natural Resources

NB-1   Limestone from Havelock Lime Works, Samphill quarry,
       from a 10 t shipment to CCRL, 1980.

NB-1-3   Limestone from CCRL, Canada Cement material from
         screened 8 x 20 M sample, March 1982.

NB-1-4   Limestone from "-1/4 inch" Samphill waste pile.

NB-1-5   Limestone from "-1/4 inch" Canada Cement waste pile.

NB-1-6   Limestone from Samphill quarry face.

NB-1-7   Limestone from "-3 x 1-1/2 inch" Samphill pile.

NB-1-8   Limestone from "-3/4 x 1/4 inch" Canada Cement pile.

NB-1-9   Limestone from "-1/4 inch" truckload of Samphill to CFB
         Summerside.

NB-1-10   Limestone from "-1/4 inch" truckload of Canada Cement to
          CFB Summerside.

NB-1-11   Limestone from a bag of "Shell Mix", Havelock Lime
          Works, used as the standard limestone, 1982.

NB-1-12   Limestone Samphill quarry supplied by NB Electric
          Power, Jan. 1986.

NB-1-13   Limestone from Canada Cement quarry supplied by NB
          Electric Power, Jan. 1986.

NB-2   Limestone from a quarry at Carlisle,
       Carleton County, 1981.

NB-3   Dolomite from Brookville Manufacturing Co. Ltd.,
       quarry, Brookville, Kings County, 1981.

NB-4   Limestone from Elmtree Resources quarry, near Petit
       Rocher, Gloucester County, 1981.

NB-4-2   Limestone, (Ag Lime), from Elmtree Resources, Elmtree
         quarry, supplied by NB Electric Power, Feb. 1986.

NB-4-3   Limestone from Elmtree Resources, Sormony quarry,
         also by NB Electric Power.

NB-5   Limestone from a quarry at Windsor, Carleton County, 1981.

NB-6   Limestone from Glebe Mine (ore dump near old shaft).
Supplied by N.B. Electric Power, Jan. 1986.

NB-7   Limestone from Markhamville No. 2 Shaft.
Supplied by N.B. Electric Power, Jan. 1986.

Alberta

CS-1   Limestone from outcrop on Clausen's Landing on the
Athabasca River, 1981. Supplied by C.F. Lamb,
Sr. Geologist, Canstar Oil Sands Ltd.

SY-1   Limestone from outcrop on Syncrude Canada Ltd. Property
where Beaver Creek crosses Provincial Highway 963, 1981.
Supplied by N.D. O'Donnell, Section Head, Geology,
Syncrude Canada Ltd.

SY-2   Limestone from a 50 t lot quarried 49 km north of Fort
McMurray on the west side of Highway 963, March 1983.
Supplied by D. Wallace, Alberta Research Council (ref).

Alt-4   Limestone from Steele Brothers (Canada) Ltd.,
quarry at Exshaw, 1983.

Alt-5   Supplied by B. Clements, Combustion Engineering Ltd.

Alt-6   Limestone from beneath tar sands mining pit at Suncor,
1984.

Alt-7   Limestone from Genstar Cement Ltd. quarry at Cadomin,
1984. Alt-6 and -7 supplied by D. Scoulding, Monenco
Engineers and Constructors Inc.

Table 2 - Chemical composition of sorbents (mass %)

Sample	$CaCO_3$	$MgCO_3$	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	K_2O
Nova Scotia							
GR-1 Gays River	54.4	32.6	1.36	1.37	7.14	0.23	0.24
NS-1 Irish Cove	94.4	1.00	0.31	0.32	1.20	0.03	0.02
-9 " "	94.4	1.53	0.59	0.42	2.34	0.03	0.04
-2 Kelly Cove	52.4	42.2	0.49	0.33	6.17	0.01	0.02
-3 Musquodobit	50.6	40.4	0.94	0.98	6.38	0.16	0.02
-13 "	92.8	0.32	-	-	-	-	-
-4 Brookfield	83.9	1.97	1.32	3.13	12.3	0.08	0.83
-8 "	86.3	1.00	0.87	2.63	8.33	0.06	0.66
-5 Calpo	95.6	1.99	0.21	0.22	0.99	0.07	0.05
-10 "	96.1	0.90	0.27	0.13	1.49	0.02	0.02
-6 Glencoe	86.7	10.1	0.49	0.83	3.27	0.04	0.17
-7 "	93.9	3.87	0.21	0.42	1.28	0.06	0.06
-11 "	92.1	3.84	0.44	0.59	2.15	0.01	0.17
-12 "	92.4	4.52	0.30	0.40	1.68	0.01	0.01
-14 Glendale	92.1	5.77	R203 =	1.52	1.57	0.01	0.05*
-15 East Bay I	92.3	1.47	R203 =	1.5	4.0	-	- *
-16 " " II	92.3	1.47	R203 =	1.5	4.0	-	- *
-17 Gabarus Lake	92.1	3.78	R203 =	1.4	1.6	-	- *
-18 Cape Dauphin	83.3	-	-	-	-	-	-
-19 " "	95.3	-	-	-	-	-	-
New Brunswick							
NB-1-1 Havelock	94.6	1.83	0.37	-	3.08	-	-
1-3	98.4	1.37	0.20	-	1.44	-	-
1-4	83.1	1.62	1.16	-	11.4	-	-
1-5	94.1	1.32	0.59	-	4.87	-	-
1-6	100.4	0.63	0.16	-	1.48	-	-
1-7	101.0	0.59	0.17	-	1.11	-	-
1-8	99.1	1.11	0.19	-	1.62	-	-
1-9	92.1	0.0	0.44	-	3.22	-	-
1-10	92.7	0.0	0.36	-	3.02	-	-
1-11	95.0	-	-	-	-	-	-
1-12	97.2	-	-	-	-	-	-
1-13	97.6	-	-	-	-	-	-
-2 Carlisle	98.4	1.00	0.21	0.45	0.71	0.04	0.03
-3 Brockville	54.1	45.0	0.23	0.57	1.54	0.04	0.09
-4 Elmtree	91.5	1.00	0.57	1.53	7.02	0.04	0.23
-4-2	93	-	-	-	-	-	-
-4-3	93	-	-	-	-	-	-
-5 Windsor	97.6	1.63	0.13	0.14	0.32	1.31	0.07
-6 Glebe Mine	96.5	-	-	-	-	-	-
-7 Markhamville	95.9	-	-	-	-	-	-
Alberta							
CS-1 Clausen	90.1	2.89	0.83	2.04	8.32	0.06	0.54
SY-1 Syncrude	91.3	2.49	1.00	1.34	5.98	0.03	0.23
2 "	75.6	2.50	1.59	3.93	14.4	0.04	0.93
Alt-4 Exshaw	97	-	-	-	-	-	- **
Alt-5 "	97	-	-	-	-	-	- **
-6 Suncor	65.6	-	-	-	-	-	-
-7 Cadomin	93.4	-	-	-	-	-	-

*Analysis supplied by W. Shaw.
**Analysis supplied by B. Clements.

Table 3 - Optical emission spectroscopic analysis

Element	Min. Detection limit m %	NS-1	NS-2	NS-3	NS-4	NS-5	NS-6	NS-7
Ti	0.0003	.015	.005	.02	.07	.01	.03	.01
Mn	0.0001	.7	.05	1	.02	.5	.01	.005
Ag	0.0003	-*	-	.0003	-	-	-	-
B	0.0015	-	-	.002	.005	-	.002	.0015
Ba	0.0003	.03	.0015	.005	.015	.02	.015	.002
Be	0.0001	-	-	-	.0001	.0002	-	.0001
Co	0.0001	.001	.001	.001	.001	.001	.001	.001
Cr	0.0007	-	.03	.0007	.005	.0007	.002	.0015
Cu	0.0002	.0007	.001	.0007	.005	.0007	.002	.001
Ge	0.002	-	-	.003	-	-	-	-
Mo	0.002	.003	.003	.002	.002	.002	.002	.002
Nb	0.002	.003	.003	.003	-	.002	.003	.003
Ni	0.001	.003	.007	.002	.01	.002	.002	.002
Pb	0.007	.01	.02	-	-	-	.02	-
Sc	0.0003	-	-	-	.0007	-	.0003	-
Sn	0.003	-	-	-	-	-	.003	-
Sr	0.0003	.02	.003	.005	.03	.03	.02	.01
V	0.001	-	.001	-	.002	-	-	-
Y	0.001	.001	.001	.002	.002	.005	.002	.001
Zn	0.02	.05	.02	-	.02	.02	-	-
Zr	0.001	.001	-	.003	.005	.001	.002	.001

The following elements were analyzed but not detected at the minimum detection limits:

P 0.07, As 0.03, Au 0.007, Bi 0.007, Cd 0.007, Ce 0.003, Hf 0.005, La 0.003, Nd 0.005, Sb 0.02, Ta 0.2, Te 0.2, Th 0.01, U 0.015, W 0.007, Yb 0.0002, In 0.002, Pd 0.007, Pt 0.005, Tl 0.03.
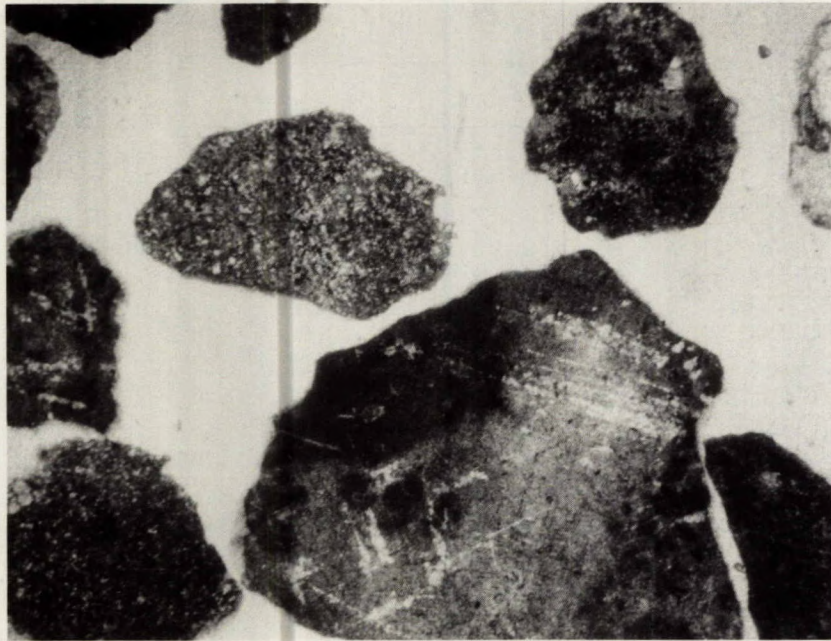
* - less than detection limit.
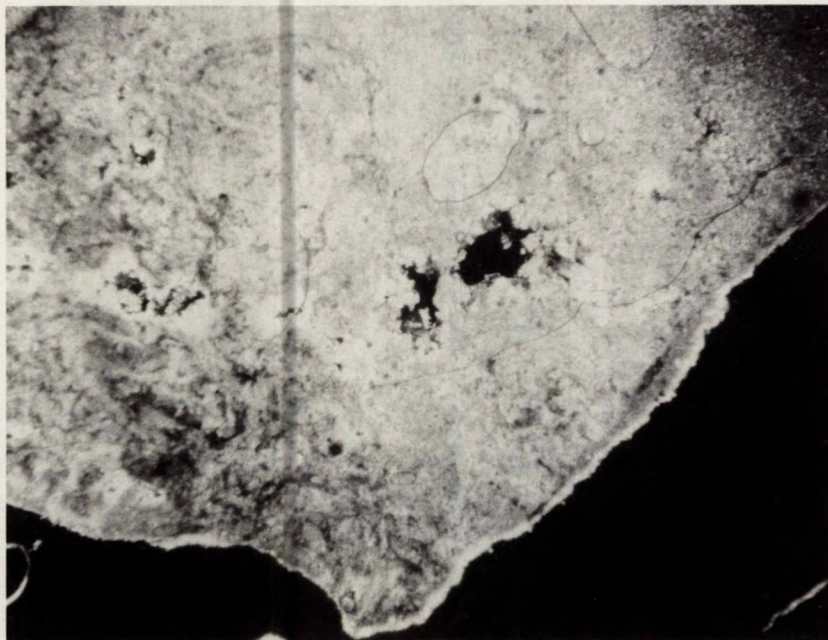
Fig 1 - Irish Cove (NS-1) limestone, 30x

Fig. 2 - Calpo (NS-10) limestone, 30x

Fig. 3 - Glencoe (NS-12) limestone, 30x

FLUIDIZED-BED REACTOR TEST PROCEDURE

Fluidized-Bed Reactor

A bench-scale fluidized-bed reactor, a schematic of which is given as Figure 4, was designed and built to test the SO_2 capture capacity of sorbents. The reactor is 53 mm i.d. (2 inch, schedule 40 pipe) type 316 stainless steel that was used because it was readily available, although for improved corrosion resistance at high temperature, type 310 would have been the preferred alloy. The reactor is made of two pipes, the upper being 1100 mm and the bottom section 350 mm, each pipe being flanged at both ends. The internal diameter of the top flange of the bottom section was machined to accept a 60 mm diameter by 4.6 mm thick porous silica disc, 40-90 μm porosity, which is used as the gas distributor. The lower pipe is filled with ceramic saddles and is used as a preheater. Four pairs of 305 mm long, half-shell resistance heaters, each heater being 1130 watt, and each pair with their own thermocouple and proportional controller are used to provide uniform heating to the reactor. Bed temperature is monitored with a thermocouple approximately 30 mm above the distributor. With a 250 g sand bed, heat-up time to 850°C is approximately one and a half hours.

Material is added to the reactor from a hopper by gravity. Following a run, it is removed with a vacuum system that withdraws all the bed material via a 9.5 mm diameter tube whose open end is 3 mm above the distributor. Dust is collected by a cyclone on the exhaust line.

A synthetic flue gas is made by metering the respective quantities of CO_2, O_2, and N_2 through rotameters. An electronic mass flow controller is used to control the precise quantity of SO_2. All the gases are combined through a mass flow meter to measure the total flow to the reactor. There is a bypass so that the gas concentrations can be measured before and after passing through the reactor. The analyzers used are a Beckman Oxygen Analyzer Model 755, an Infrared Industries Dual Analyzer for CO and CO_2 Model 702, and a Beckman Infrared SO_2 Analyzer Model 865. All may be connected to chart recorders although usually only the SO_2 concentration is recorded. The composition of the synthetic gas is 8% CO_2, 5% O_2, and 0.28% SO_2, with the balance being N_2. This composition, which is typical of the gas composition within the bed, is maintained for all test work.

Manometers measure the gas pressure to the reactor and the pressure drop across the reactor. Under standard test conditions these values do not vary from run to run. Any variation indicates a problem such as a damaged distributor or a major leak in the system.

The bed material is ASTM C-109 standard, graded pure Ottawa silica sand. This is a round-grained sand with an average particle size of 400 μm. With a 250 g sand bed, the minimum fluidizing velocity at 22°C was determined as 20 cm/s. The gas flow to the reactor is 18.9 L min, which gives a superficial velocity of 54 cm/s at 850°C. The gas residence time, determined by dividing the expanded bed height by the superficial velocity, is 0.5 s.

For each test the reactor is heated to 850°C, with a bed of 250 g sand fluidized with air or nitrogen. Prior to adding any sorbent to the system, the synthetic flue gas is admitted and a trace of the SO_2 concentration through

the reactor and by-passing the reactor is obtained on the chart recorder. The SO_2 concentration through the reactor is lower than the bypass reading. The change in SO_2 concentration is caused by the reaction

$$SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$$
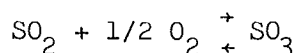
which appears to be catalyzed by the hot stainless steel reaction tube and whose equilibrium ratio of SO_2/SO_3 is 0.117 at 850°C and 5% O_2. (With a quartz or refractory tube, the reaction kinetics are too slow to form any observable quantities of SO_3.) Since the infrared SO_2 analyzer does not respond to SO_3, the readings are about 11% low.

A weighed, usually 10 g, sieved sample of limestone or dolomite is added to the reactor from a hopper at the top. The temperature drops approximately 15°C but recovers to 850°C within 10 minutes. Within a minute of adding the sample, the SO_2 concentration in the exhaust gas drops to a fraction of the inlet concentration. It then begins to increase at a rate that depends upon the sulphation characteristics of the sorbent, until after one to three hours the exhaust concentration is constant at or very near to the inlet concentration. Since the SO_3 concentration cannot be measured, it is assumed that the reaction of SO_3 with the sorbent is the same as with SO_2. In fact, SO_3 is more reactive (17), but the error due to the assumption should not be more than a few per cent. A typical curve of the SO_2 concentration recorded during a test is given in Figure 5. With the area above the curve representing the SO_2 captured by the sorbent, the per cent sulphation, X %, versus time for the sample can be calculated using Simpson's Rule:

$$X\ \% = \frac{\text{area } SO_2 \text{ captured} * \text{mol } SO_2/\text{min input} * t(\text{min})}{\text{area } SO_2 \text{ input} * \text{mol Ca}} \qquad \text{Eq 1}$$

A reiterative, non-linear least squares computer program fits the following empirical equation to the sulphation data:

$$X\ \% = a(1-\exp(-kt^n)) \qquad \text{Eq 2}$$

As will be discussed later, the parameters a, k, and n are used in a model for predicting sorbent performance.

Thermogravimetric Analysis (TGA)

The sulphation characteristics of nineteen limestones were assessed by Dr. Irving Johnson, Clarendon Hills, Illinois, using thermogravimetric analysis techniques. This work was done under two contracts, the first for Nova Scotia Power Corporation to test four limestones and the second covering the remainder of the samples by CANMET (18). The contracts encompassed thermogravimetric analysis of the rocks, predictions of sorbent performance using the ANL model, and determination of rock decrepitation.

In the thermogravimetric analysis method, 0.3 to 0.4 g of 850-1000 μm rock is calcined to 850°C in an atmosphere of 20% CO_2, balance N_2, until a constant weight loss is obtained. A synthetic flue gas containing 0.3% SO_2 is then

Fig. 4 - Bench-scale fluidized-bed reactor
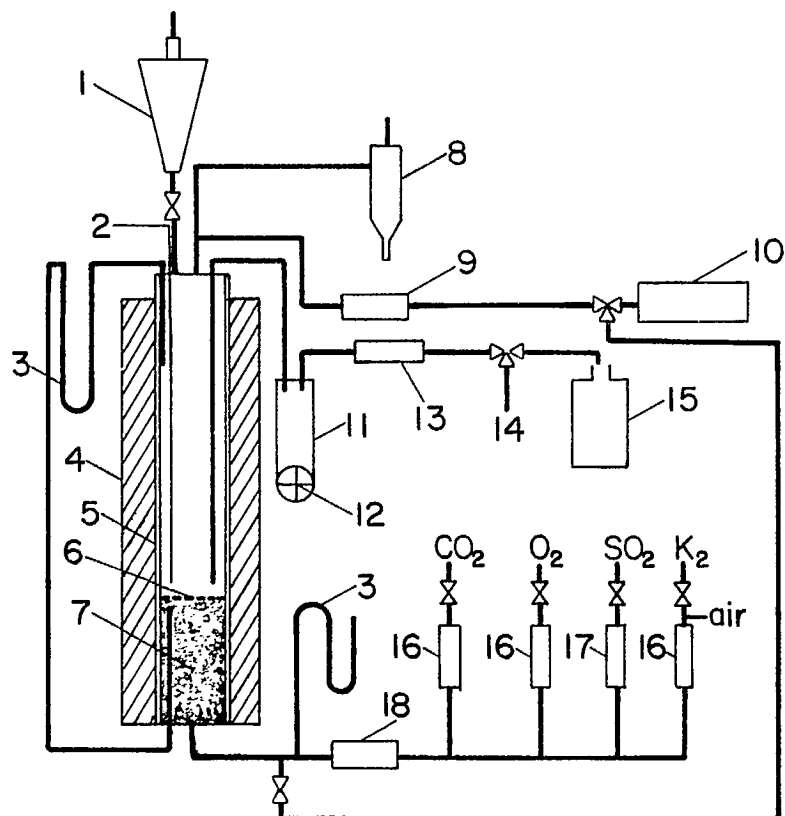
1 Feed hopper
2 Thermocouples
3 Monometer
4 4 Pairs resistance heaters
5 316 Stainless tube
6 Porous quartz distributor
7 Preheated packing
8 Cyclone
9 Purmapure filter and dryer

10 Beckman 865 SO$_2$ analyser
11 Sample receiver
12 Ball valve
13 Filter
14 Vacuum pump
15 Vacuum reservoir
16 Flow meters
17 Electronic mass flow controller
18 Electronic mass flow meter
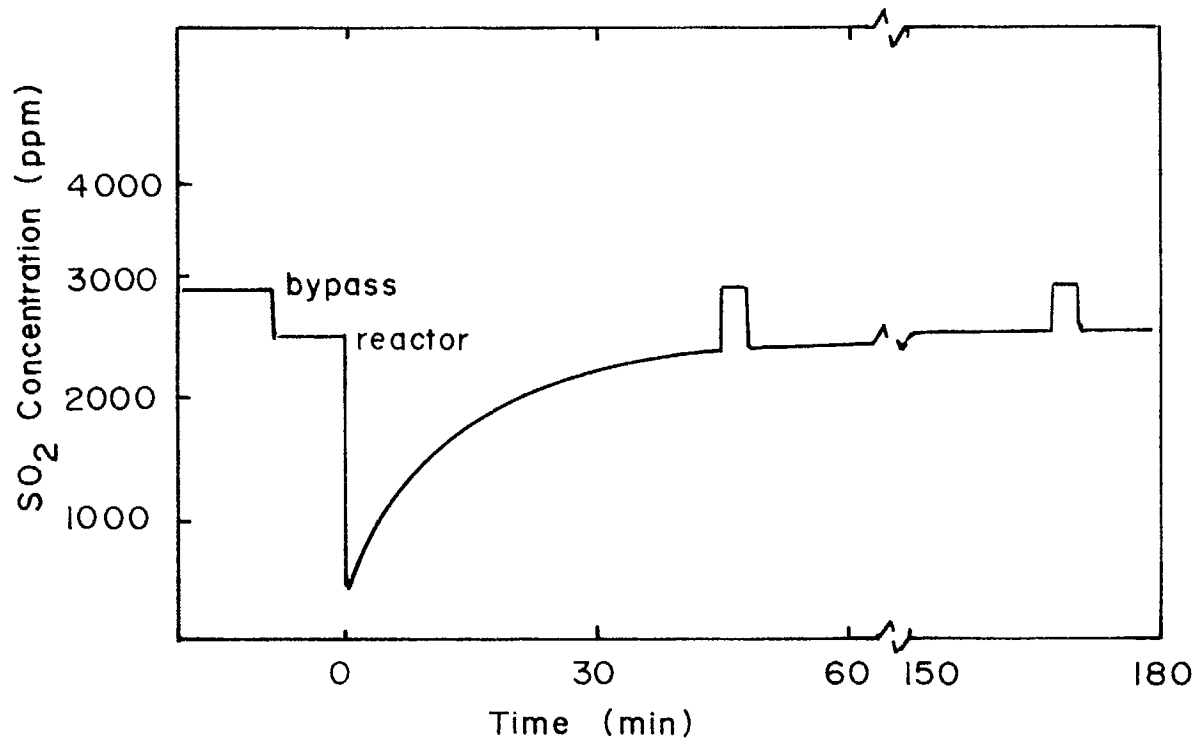
Fig. 5 - Typical SO$_2$ emission curve

passed over the sample, while the weight gain due to sulphation is measured with time (19). This sulphation curve has the same shape as that calculated from the fluidized-bed reactor data and fits the same Equation 2.

FLUIDIZED-BED REACTOR TEST RESULTS

Calibration of the FBR

The sulphation capacity of a limestone, as determined in the fluidized-bed reactor, is independent of the quantity of material added to the reactor. Assuming that the particle size of the limestone and the composition of the flue gas are kept constant, then an increased quantity of sample will simply increase the total time required to sulphate the sample. Thus, in equation 2, the value of "a" is independent of sample quantity; however, the parameters "k" and "n" are dependent, as illustrated by results of sulphation tests on various quantities of NB-1 limestone given in Table 4. Because the parameters of the 10 g sample in the FBR so closely matched the parameters of the TGA curve, this sample mass was taken as the standard of all tests.

An error in the calculated moles SO_2/min, which was not discovered until partway through the program, resulted in the previously calculated "a" being 8% low. Therefore, in all previous reports on this work the values of "X" and "a" should be corrected by multiplying by 1.08 (13,20-22).

A graph of the sulphation curves is given in Figure 6. To make the comparison of the curves easier to visualize, the value of "a" has been set as 30.0 for all samples. It is seen that the sulphation curve of a 10 g sample lies very close to that determined by the TGA. A more complete comparison of TGA and FBR curves will be given later.

Table 4 - Effect of sample mass on sulphation curve parameters
850-1000 μm Havelock (NB-1) limestone

Sample mass	a	k	n
50 g	29.1	0.01345	1.0275
35 g	29.9	0.02137	1.0027
25 g	29.2	0.03209	0.9466
10 g	30.7	0.05630	0.8384
TGA	28.4	0.05372	0.8831

Samples of Havelock limestone are used as an internal standard to ensure reproducibility of the FBR technique. Initially NB-1, from a 10 t shipment to CCRL, was used as the standard; however, for the past two years a 40 kg bag of Havelock "Shell Mix" (NB-1-11) has been the source of limestone for the internal standard. The value of NB-1 in Tables 5 and 6 represents an average of 10 tests that yield a sulphation capacity of 33.0%, with a standard deviation of 2.5%. Excluding the one test with the largest difference from the average, the standard deviation decreases to 1.2%. Twenty-three tests of NB-1-11 have averaged 33.5% sulphation, with a standard deviation of 2.1%.

Fig. 6 - Sulphation curves of Havelock (NB-1) limestone for 10, 25, 35, and
50 g samples in the FBR versus TGA

Sulphation Capacity of Sorbents
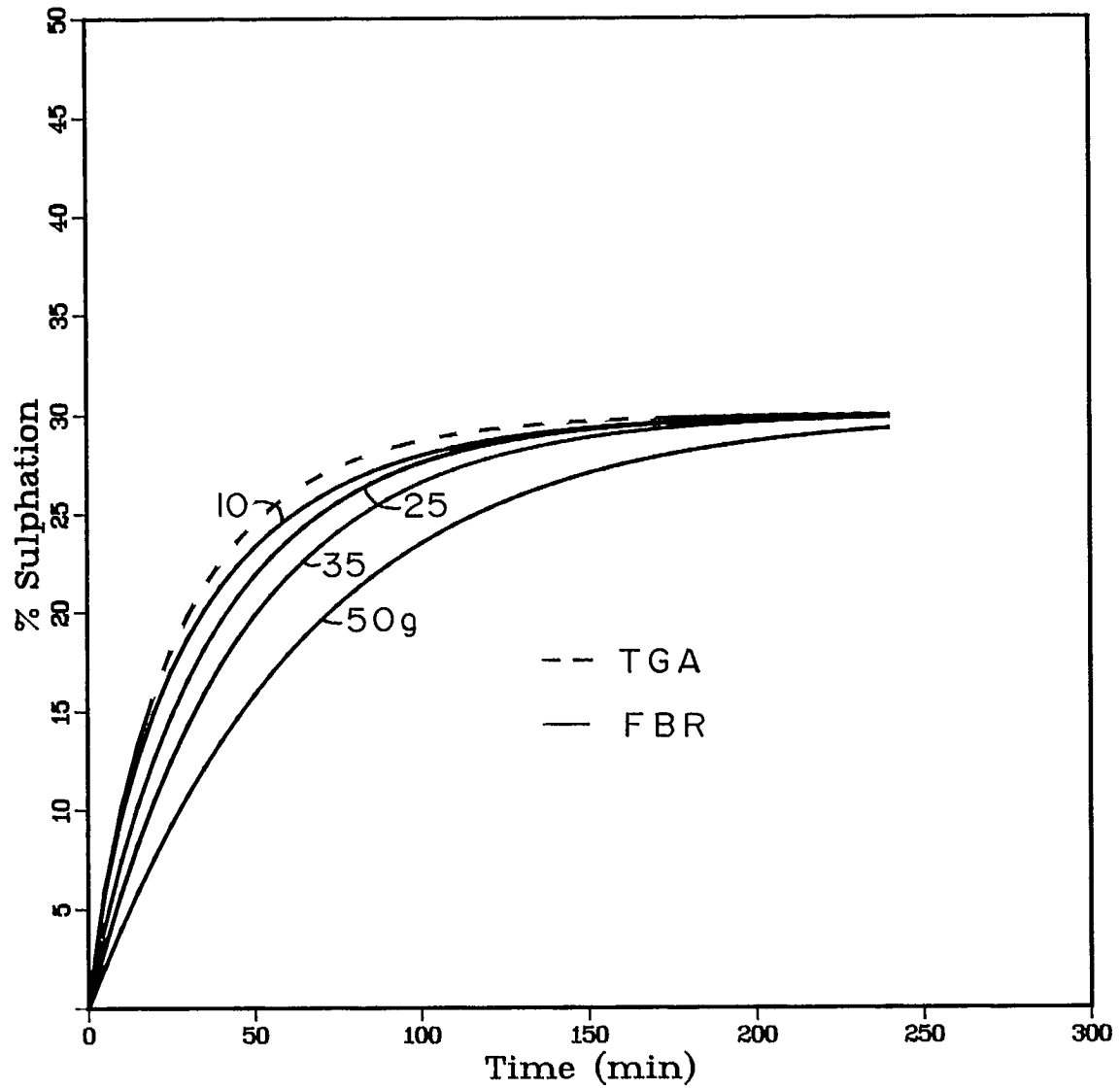
All of the limestone and dolomite samples were tested in the 850-1000 μm
size fraction in the FBR and 19 of them in the TGA. Additionally, in some
tests the sulphated limestone was separated from the sand bed and analyzed for
calcium and sulphur. This size fraction is commonly used in sorbent evalua-
tions and is considered representative of the particle-size distribution in
most bubbling atmospheric fluidized-bed systems. The sulphation curves (Fig-
ures 7-10) make it possible to compare the sulphation capacity of all the sor-
bents and to rank them according to their ability to capture sulphur dioxide.
The parameters of Equation 2 for the sample are used for modelling. Table 5
gives the sulphation capacity of the samples as determined by the FBR, TGA,
and chemical analysis.

As can be seen from Table 5 and Figures 7-10, there is a wide variation in
the sulphation capacity of the limestones and dolomites tested. Of the Nova
Scotia sorbents, the Calpo sample (NS-10) has the highest sulphation, although
there is considerable difference, 34 versus 55%, between the two samples (NS-5
and 10) taken eight months apart. The Gabarus Lake limestone (NS-17) with a
sulphation capacity of 33% and East Bay limestones (NS-15 and 16) are very
good sorbents, although there is some difference between the two latter
samples (located about 1 km apart in the deposit) at 27 and 37% sulphation.
The limestone sample from Upper Musquodobit (NS-13) is also very good at 32%
sulphation. The dolomite sample (NS-3) from the same deposit sulphated to 25%
but since it contains only 50% $CaCO_3$, its efficiency per mass is rather low.
Kelly Cove (NS-2) is also a dolomite and sulphates poorly. Irish Cove (NS-1
and 9) is fairly good limestone. The two Brookfield samples (NS-4 and 8),
which were collected at the same time but shipped in different containers and
hence given different numbers, are poor sorbents. The four samples from
Glencoe (NS-6 and 7, NS-11 and 12) sulphate in the low 20% range. The Glencoe
deposit, which is more than 200 million tonnes, is probably the largest lime-
stone deposit in Nova Scotia (23) so four samples, even though two are drill
core samples, do not represent the entire deposit. The Glendale and Cape
Dauphin deposits (NS-14) behave in a similar manner to Glencoe.

Havelock limestone (NB-1) is the best New Brunswick limestone. Limestones
from the two quarries utilized by Havelock Lime Works have been evaluated more
frequently than from any other source. Twelve samples tested over a five-year
period yielded sulphation capacities from 27 to 35%, the average being 30.3%
for all the samples. There has been no detectable increase or decrease in
sulphation capacity over the time period. The sulphation behaviour is essen-
tially the same for both quarries, that is, the Canada Cement quarry at
Havelock and the Samphill quarry 8 km away.

Of the other New Brunswick limestones, the Elmtree (NB-4) Petit Roche samples
have the lowest sulphation, 19%. Brookville (NB-3) is a dolomite so its
effective sulphation capacity on a mass basis is about half the 27% value.
Glebe Mine (NB-6) and Carlisle (NB-2) sulphate to the mid-twenties.

All of the limestones from Alberta sulphated in the low to mid-twenties range.
Those from Exshaw (Alt-4 and 5) were the lowest at about 20% followed by
Cadomin (Alt-7) at 22%. Both deposits lie in the same geological formation
in southwestern Alberta. Clausen's Landing and Suncor were both 26% but the
Suncor sample contained only 66% $CaCO_3$. The two samples designated Syncrude

Table 5 - Sorbent sulphation capacity, % X, 850-1000 μm particles

Sample		FBR	TGA	Chem Anal
NS-1	Irish Cove	27.2	20.5	30.7
9	" "	25.1	24.8	30.8
2	Kelly Cove	18.4	22.4	-
3	Musquodobit	24.6	25.7	-
13	"	32.3	-	-
4	Brookfield	16.0	16.7	-
8	"	17.7	19.8	-
5	Calpo	33.9	33.8	-
10	"	51.8	42.1	45.9
6	Glencoe	23.2	25.5	23.8
7	"	21.9	24.9	20.9
11	"	21.2	26.3	20.7
12	"	18.0	23.6	19.9
14	Glendale	23.7	-	-
15	East Bay 1	27.2	-	-
16	" " II	37.0	-	-
17	Gabarus Lake	33.2	-	-
NB-1	Havelock	33.0	29.9	29.0
2	Carlisle	25.3	20.8	25.1
3	Brookville	26.7	31.4	27.6
4	Elmtree	19.1	14.2	-
4-2	" Petit Rocher	18.9	-	-
4-3	" Sormony	22.8	-	-
5	Windsor	25.9	17.7	-
6	Glebe Mine	27.2	-	-
7	Markhamville	21.9	-	-
CS-1	Clausen's Landing	26.2	21.8	-
SY-1	Syncrude	22.0	19.3	25.1
2	"	24.1	-	-
ALT-4	Exshaw	20.0	-	-
5	"	19.4	-	-
6	Suncor	26.2	-	-
7	Cadomin	22.3	-	-

Note: The FBR data are the average of 2-5 tests.
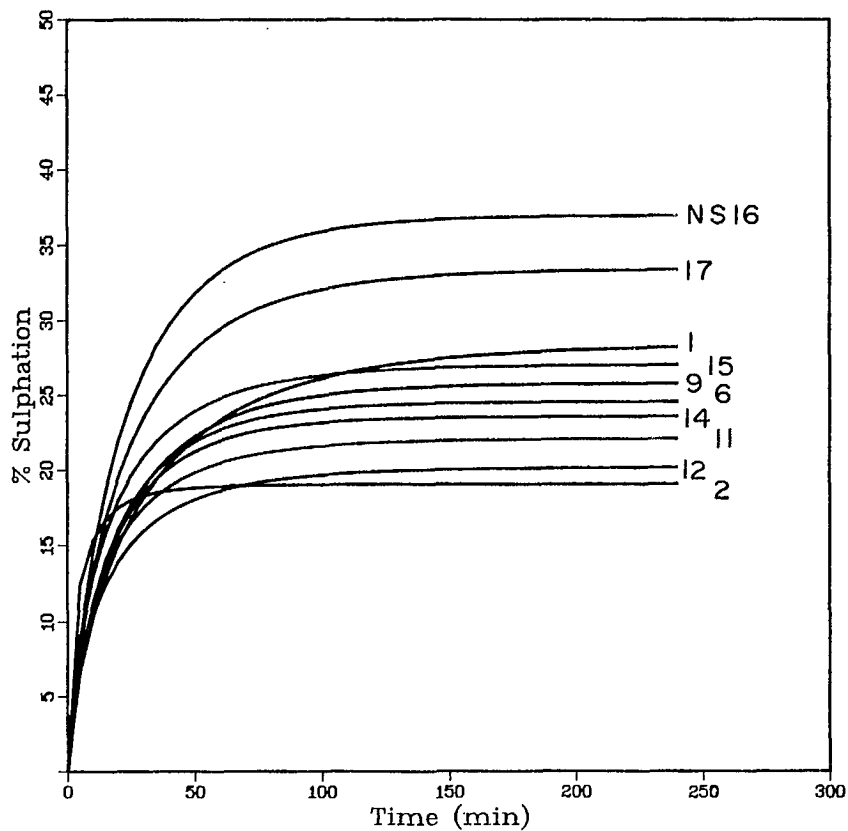
Fig. 7 - Sulphation curves for Cape Breton Island, Nova Scotia sorbents, 0.28% SO_2, 850°C, 850-1000 μm
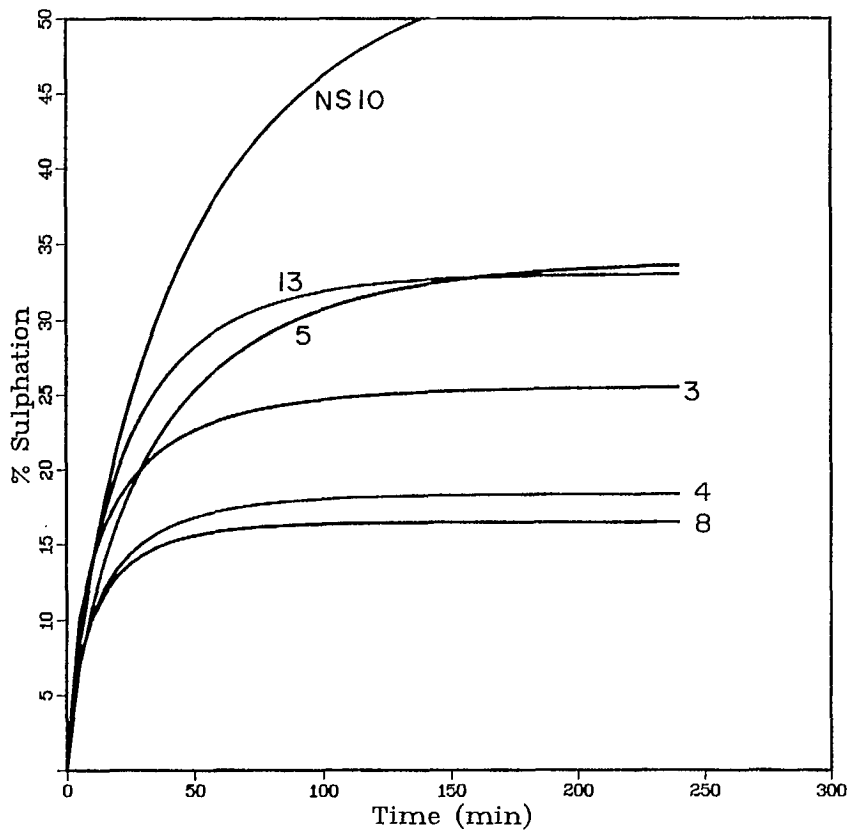

Fig. 8 - Sulphation curves for mainland Nova Scotia sorbents, 0.28% SO_2, 850°C, 850-1000 μm
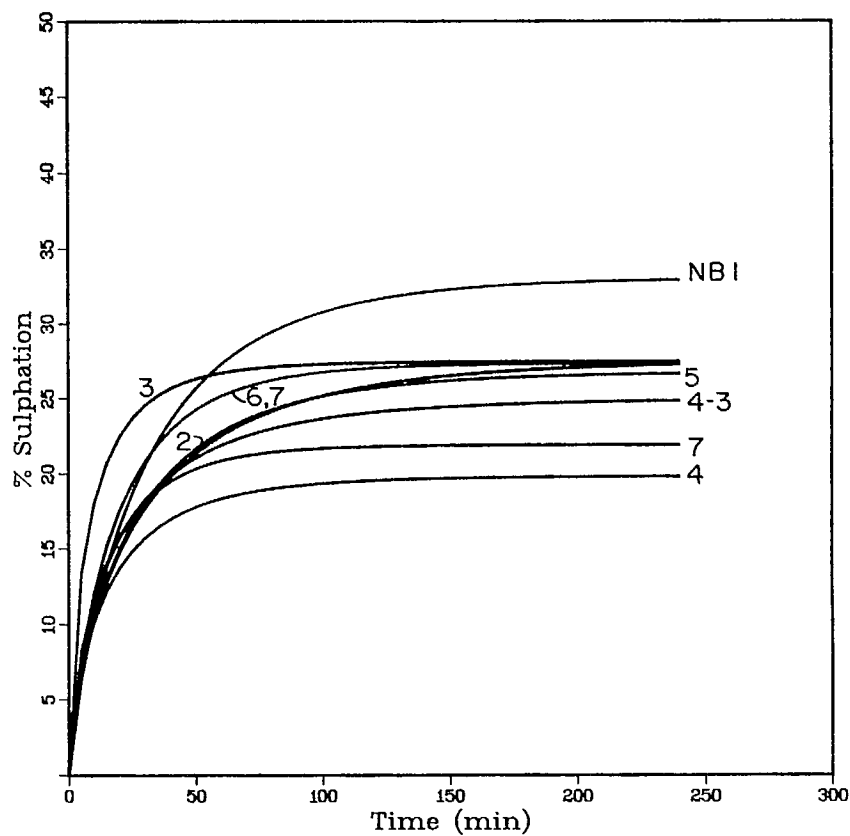
Fig. 9 - Sulphation curves for New Brunswick sorbents, 0.28% SO_2, 850°C, 850-1000 μm
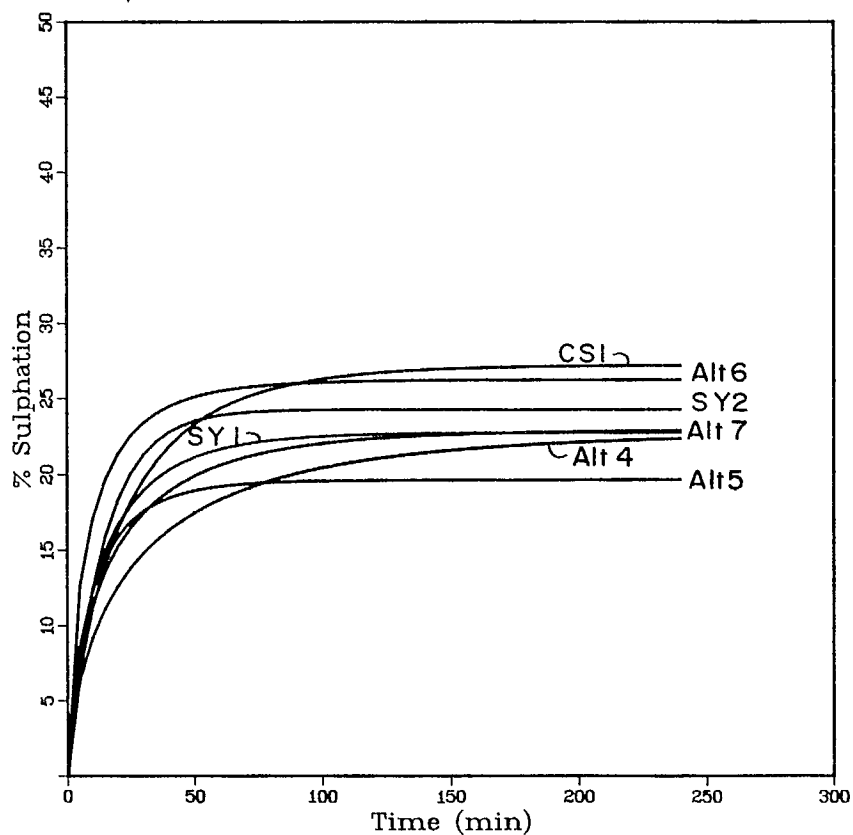

Fig. 10 - Sulphation curves for Alberta sorbents, 0.28% SO_2, 850°C, 850-1000 μm

(SY-1 and 2) are both from the same deposit. The first is a surface out-crop sample analyzing 91% $CaCO_3$, and the second analyzing 76% $CaCO_3$ represents 50 t quarried for AFBC tests.

Comparison of FBR and TGA Results

For most samples, the FBR and TGA results listed in Table 5 are in very good agreement. The sulphation capacities of the samples determined by both methods are plotted against each other in Figure 11. If there were perfect agreement between the two methods the data would fall on the line, whereas in fact, the average deviation from the line is 1.93% sulphation. The average sulphation of the 19 samples tested by the TGA is 24.3% compared to 25.1% for the same samples in the FBR. Although there are fewer chemical analysis data, the same approach results in an average deviation between the FBR and chemical analysis of 1.2% sulphation, and between the TGA and chemical analysis of 2.3%.

That there are some differences in the results of the two methods is hardly surprising. That there is not a greater difference is perhaps more surprising, if the differences in the two methods are considered. In TGA the lime-stone is brought from room temperature to 850°C in an atmosphere of 20% CO_2/N_2, which would tend to promote the formation of an open pore structure with subsequent enhanced sulphation capacity (2). Thermal decrepitation of the sample in the pan would result in smaller particles, increased surface area, and improved sulphation. In the FBR the sample suffers thermal shock, simultaneous calcination and sulphation, and attrition. Thermal shock may cause some sorbent samples to break into smaller fractions. Small particles will improve sulphation, but if the particles are too fine they may be elu-triated from the reactor before complete sulphation has occurred. Attrition with the sand bed may remove some of the sulphated layer from partially sul-phated sorbent to allow sulphation to continue. Thus, there are different forces affecting the sulphation behaviour in the two methods. It is interest-ing to note that the results from the chemical analysis are closer to those of the FBR than the TGA.

Table 5 compares only the sulphation capacity determined by the three methods. The following Table 6 lists the results for all sorbents tested and compares the parameters "a", "k", and "n" of the sulphation curve Equation 2 for the samples tested by both methods.

The parameter "a" equals the maximum sulphation capacity a sorbent can achieve in infinite time under the standard test conditions. It is usually very close to the value of "X", the sulphation capacity determined in the test.

The other curve-fitting constants are "k" and "n". Graphs comparing the values of "k" and "n" from the TGA and FBR are given in Figures 12 and 13. There is reasonable agreement of the "k" values for most samples, although a few are completely different. There does not appear to be much agreement in the values of "n". For the TGA, "n" averages 0.61 and varies from 0.2 to 1, whereas for the FBR it lies between 0.6 and 0.8 and averages 0.72. Fee et al. (7) reported an average value of "n" as 0.76 with a range of 0.6 to 1.1 for the various sorbents studied by ANL. If "n" is unity, the rate of calcium

Table 6 - Sulphation curve parameters

| Sample	FBR			TGA		
	a	k	n	a	k	n
NS-1	28.45	0.0787	0.7519	20.33	0.0944	0.7050
-9	25.80	0.0838	0.8087	25.16	0.1244	0.5875
-2	19.05	0.3907	0.6178	26.61	0.2416	0.3796
-3	25.61	0.1809	0.6320	25.49	0.2085	0.5453
-13	33.08	0.0845	0.7978	-	-	-
-4	16.49	0.1912	0.6933	17.31	0.6226	0.2442
-8	18.39	0.1701	0.6799	19.57	0.0913	0.8633
-5	34.09	0.0627	0.7869	33.58	0.0650	0.8317
-10	53.55	0.0441	0.8049	41.14	0.0277	0.9862
-6	24.57	0.0955	0.8035	26.23	0.2556	0.4564
-7	24.13	0.0956	0.6565	24.50	0.0796	0.7998
-11	22.12	0.1303	0.7307	26.46	0.1507	0.5746
-12	20.20	0.1380	0.7124	24.14	0.1634	0.5206
-14	23.60	0.0976	0.8078	-	-	-
-15	27.06	0.1165	0.7460	-	-	-
-16	36.97	0.0693	0.8547	-	-	-
-17	33.44	0.0778	0.8069	-	-	-
NB-1	33.03	0.0563	0.8384	28.38	0.0537	0.8831
-1-11	33.65	0.0725	0.8156	-	-	-
-2	26.75	0.0859	0.7559	21.97	0.4995	0.2818
-3	27.45	0.2250	0.6756	46.97	0.1436	0.4596
-4	19.80	0.1395	0.7133	14.64	0.2851	0.4596
-4-2	18.93	0.1972	0.5324	-	-	-
-4-3	22.86	0.1437	0.6556	-	-	-
-5	27.52	0.0889	0.7203	17.53	0.1083	0.6996
-6	27.33	0.0895	0.8151	-	-	-
-7	21.89	0.1143	0.8024	-	-	-
CS-1	27.25	0.0838	0.8008	21.26	0.0956	0.7264
SY-1	22.92	0.1478	0.6687	18.87	0.1467	0.6293
SY-2	24.26	0.0780	0.9669	-	-	-
ALT-4	22.73	0.1176	0.6445	-	-	-
ALT-5	19.65	0.1674	0.7650	-	-	-
ALT-6	26.27	0.2192	0.6780	-	-	-
ALT-7	22.74	0.1387	0.7526	-	-	-
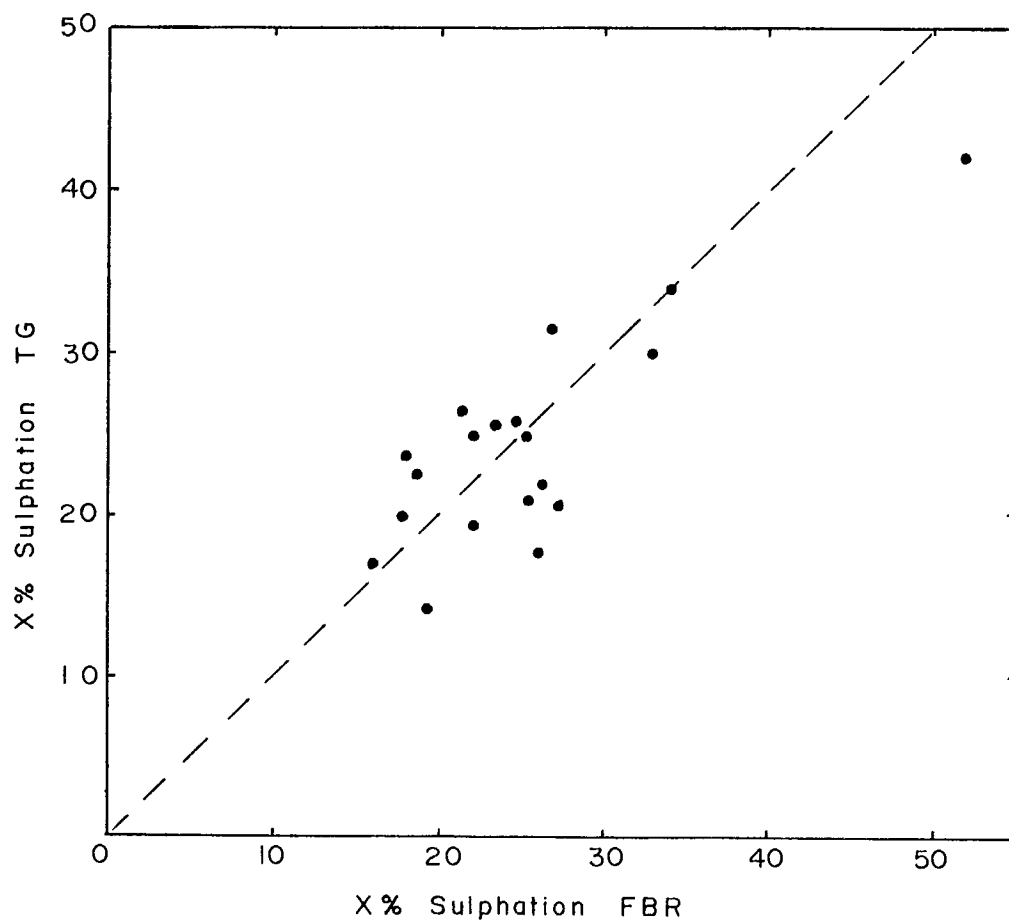
Fig. 11 - Comparison of sulphation capacity of sorbents determined by TGA and
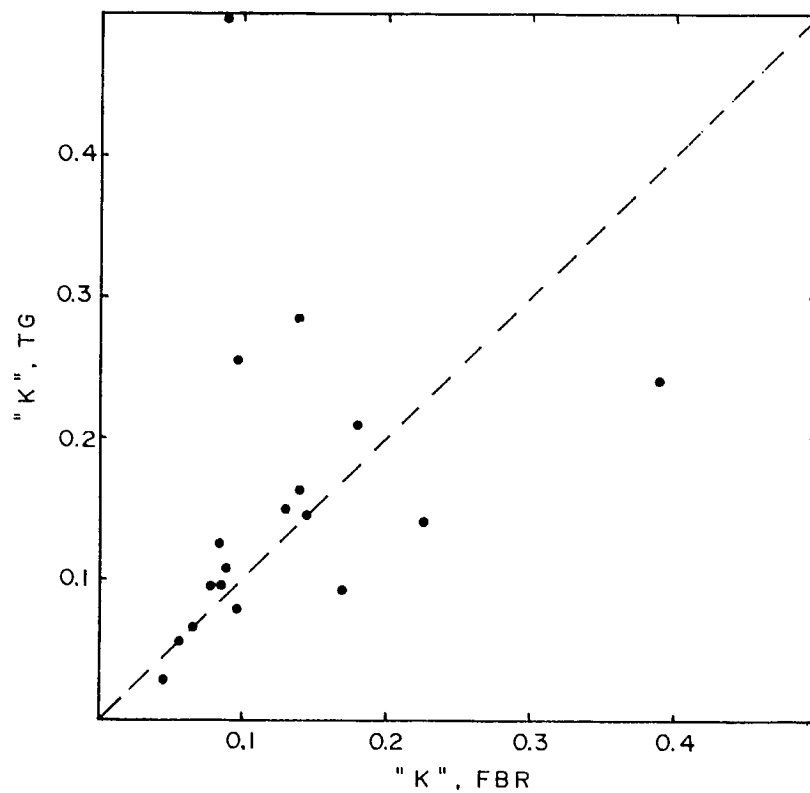FBR

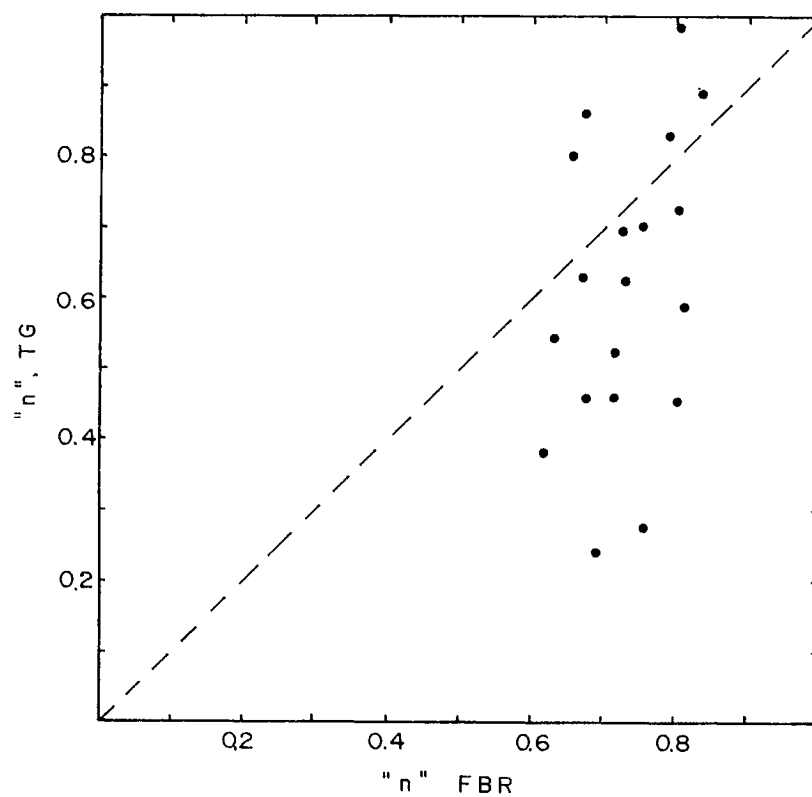Fig. 12 – Comparison of "k" parameter of sulphation curves by TGA and FBR

Fig. 13 – Comparison of "n" parameter of sulphation curves by TGA and FBR

utilization decreases linearly as the extent of calcium utilization, "a", increases. For values other than one, the rate also decreases as the calcium utilization increases, but not linearly.

An indication of the effect of varying "n" and "k" on the sulphation curves is illustrated in Figure 6, where the values change with varying sample size. A graph comparing the TGA and FBR sulphation curves of some samples is shown in Figure 14. The particular samples were chosen because the values of "a" are similar in both methods and therefore the curves are easier to compare.

Effect of Particle Size

The standard particle size for evaluating limestones is 850-1000 μm, which represents the average size in an AFBS. Because the sulphation reaction occurs at the surface and in the pores of the particle, the smaller the particle the greater will be the overall sulphation capacity of a mass of sorbent. A series of New Brunswick limestones, collected in 1986, were evaluated with respect to size fraction. The size fractions smaller than 48 mesh were pelletized with 1-2% bentonite binder so the material would not be elutriated from the bed. There was some loss from these samples by attrition, so the sulphation capacity of the smaller fractions is probably too low. The results are given in Table 7 and graphically represented in Figure 15.

The data are graphed on a semi-log scale and suggest an approximately exponential relationship for sulphation capacity versus average particle size. There is roughly a 50% increase in the sulphation capacity from the largest to the smallest size fraction.

In some tests the sulphated limestone sample was separated from the sand bed by sieving, the sand being slightly finer than most of the sulphated samples, and then analyzed for calcium and sulphur. The resulting calculated sulphation was considerably higher, particularly with the finer particle sizes, than that determined by the FBR. It would therefore appear that there was some loss of material by attrition and elutriation, especially from the pellets, which resulted in low sulphation capacities from the FBR data.

Table 7 - Sulphation capacity versus particle size
for New Brunswick limestones

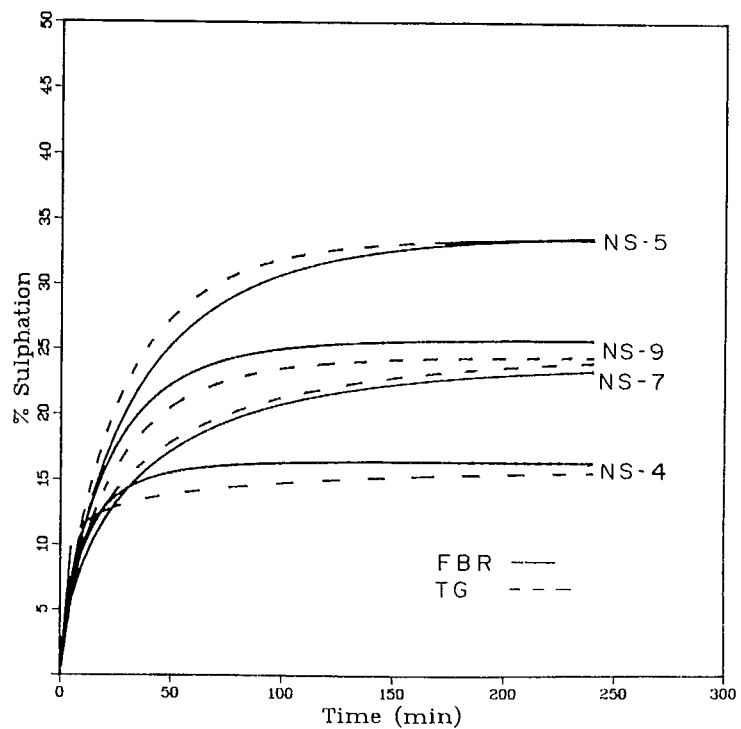| Sample	Size range						
(mesh)	16*20	20*28	28*48	48*65	65*100	100*200	200*325
Avg diam, μm	920	718	446	253	180	112	59
NB-1-12	29.0	30.0	28.4	31.4	35.4	32.6	37.0
-1-13	30.8	35.5	35.0	38.2	39.8	46.6	45.1
-6	27.2	-	29.7	-	-	-	37.3
-7	21.9	24.9	25.4	-	27.1	-	31.8
-4-2	18.9	18.2	19.6	20.3	20.3	25.4	32.6
-4-3	22.9	23.4	25.1	20.3	-	24.1	31.8

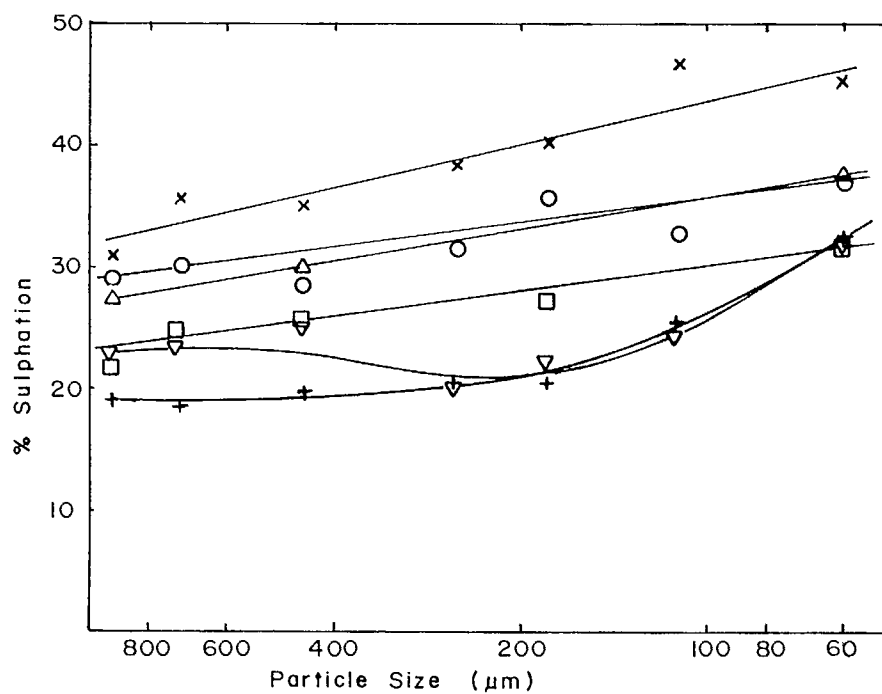Fig. 14 - Comparison of sulphation curves from TGA and FBR data

Fig. 15 - Sulphation capacity of New Brunswick limestones versus particle size

Attrition

Attrition is a term used to cover the loss or elutriation of material from the bed due to breakdown of sorbent particles. Decrepitation, thermal shock shattering, fragmentation during calcination and sulphation, abrasion of particles with each other and with the combustor tubes and walls, all of which contribute to the loss of sorbent. The amount of attrition is dependent upon some, as yet poorly defined, properties of the sorbent and upon some operating parameters of the FBC (24). Argonne National Laboratories investigated attrition with closely sized samples in both hot and cold fluidized-bed tests (25). When raw limestone was charged to a 900°C, 5 cm diameter, empty test bed and fluidized with a gas containing SO_2 it was found that the greatest particle size decrease occurred within the first ten minutes. The attrition rate increased with increasing fluidizing velocity and also with increased bed depth. Sulphation of a sorbent may decrease its attrition rate, presumably due to the formation of a harder $CaSO_4$ layer as compared to the softer calcined lime, CaO. The $CaCO_3$ content does not appear to have an influence but greater quantities of impurities, Al, Fe, and Si, may produce limestones more resistant to attrition. Moisture within the stone may cause it to be a "popper", that is, to break up excessively. It appears impossible to predict a limestone's resistance to attrition other than by testing and comparing the results with other samples.

As part of his contract, Johnson performed a shock calcination test to measure decrepitation. In this test 3-4 g of washed and sieved material, 850-1000 μm, was placed in a furnace preheated to 870°C. The stone reached furnace temperature within 1.5 min. After 20 min it was removed, allowed to cool in air, weighed, and sieved through the 850 μm screen. The quantity of material passing the sieve is a measure of the decrepitation. The results of Johnson's shock calcination tests are given in Table 8.

In the fluidized-bed reactor, dust from the breakdown of particles is collected by a cyclone on the exhaust line. With a 10 g test sample there is insufficient dust collected for an accurate determination of attrition. However, in an earlier test series in which 50 g of 212-850 μm sized limestone was used, the cyclone dust was collected and weighed. This small cyclone did not collect all of the dust and there was a considerable variation in the quantity collected in replicate tests on the same material. In fact, the mass could vary by a factor of two or more between the high and low values for the same limestone, so the results should be considered only as a semi-quantitative measure of attrition. The results of the shock calcination test and attrition in the FBR are given in Table 8.

Table 8 - Attrition test

Sample		Shock calcination % - 850 μm/initial mass	FBR % dust/initial mass
NS-1	Irish Cove	0.4	5.5
-9	" "	1.2	3.4
-2	Kelly Cove	4.9	26.4
-3	Musquodobit	0.2	2.4
-4	Brookfield	0.6	3.2
-8	"	0.3	2.9
-5	Calpo	0.2	5.7
-10	"	0.1	4.9
-6	Glencoe	2.0	7.1
-7	"	0.5	6.1
-11	"	2.6	6.4
-12	"	5.2	7.1
NB-1	Havelock	0.3	4.6
-2	Carlisle	1.1	6.1
-3	Brockville	0.8	19.2
-4	Elmtree	3.9	5.5
-5	Windsor	0.1	4.3
CS-1	Clausen	0.4	0.5
SY-1	Syncrude	0.4	2.0

In the shock calcination test the highest decrepitation was found for NS-12, NS-2, and NB-4, being from 5.2% to 3.9%. Although 5% is fairly high for this test, Johnson did not consider the breakup to be excessive for practical use. The FBR tests identified two samples, both of which were dolomites, that exhibited much higher than average attrition: NS-2 (26%) and NB-3 (19%). The greater portion of the dust was elutriated within minutes of the sample being injected into the reactor. These dusts were composed principally of unreacted material, that is, sulphation occurred to only a few per cent. The particle size distributions of the dust from one of the dolomites with a high attrition rate and from a limestone with a low rate were determined. The average particle size for the dolomite was much coarser at 96 μm than the limestone at 30 μm. This is consistent with the fact that the dolomite broke up into smaller particles as a result of thermal shock, while the surface material of the limestone abraided as fine powder over the duration of the test.

The agreement between the two methods of determining attrition is not very good, although NS-2 was identified as high by both. Franceschi et al. (24) identified thermal shock as the major cause of attrition. It is probable that the FBR provides the more severe test for determining attrition.

EFFECT OF COAL ASH ON SO$_2$ SORBENT UTILIZATION

Silica sand is used as the inert bed material to which limestone is added in the FBR test procedure. There is no evidence that the lime reacts with this sand and therefore it does not affect the sulphation behaviour of the sorbent. However, there is evidence that the fuel, or more specifically the fuel ash, may have an influence on the sulphation behaviour of the limestone. Fee et al. (7) conducted TGA tests on limestone in the presence of coal ash and reported an increase in the sulphation capacity of 40% or more over limestone alone. They attributed the increase to the beneficial effects of alkali and chloride present in the ash because these elements are known to increase sulphation (26). They also suggested that the Fe_2O_3 in the ash could have a catalytic effect on the CaO-SO$_2$ reaction. Desai et al. (27) reported improved sulphation with the addition of iron compounds to limestone.

To evaluate the effect of ash on sulphation capacity of limestone, the sand bed was replaced with coal ash and the limestone sulphation evaluated in the usual manner. Ash from nine coals was tested. To determine its effect as a catalyst, Fe_2O_3 was blended with finely ground limestone and pelletized for sulphation testing.

Limestone Samples

Three limestone samples were used for these tests: one Havelock (NB-1-11) and two Syncrude (SY-1 and SY-2). NB-1-11 and SY-1 were tested as 850-1000 μm rock, and NB-1 and SY-2 as pellets. The SY-2 material was crushed and sieved to -297 μm, 85% being less than 149 μm. The Havelock was 100%-149 μm. Ferric oxide was blended with limestone in Fe_2O_3/limestone mass ratios 0.01 and 0.05 with 1% bentonite as the binder. The technique of pelletizing will be discussed in a later section.

Ash Samples

Fording, Coleman, and Highvale ash samples were obtained by combusting coal rejects or interseam material in a muffle furnace at 800°C. Coal rejects were used because they were available from another project and because they had a very high ash content of sufficient particle size. The required ash particle size was 210-850 μm, smaller ash being elutriated from the bed by the fluidizing gas. A Hat Creek sample was obtained from a fluidized-bed combustor operated at 850°C. The sample of Evans ash was also from a pilot-scale FBC, but was diluted with sand. The materials representing Minto, Devco Prince, and Novaco were from composite samples collected, for subsequent analysis, during combustion trials in the AFBC at Summerside. These three coals were combusted in a muffle furnace. Since the resulting ash was too fine to be used in the fluidized-bed reactor, it was pulverized and pelletized prior to use. The other ash samples were not analyzed per se; instead, analyses of the bulk or representative samples were used. The ash analyses are given in Table 9.

It became apparent after testing these samples that the iron oxide content of the ash had an effect on the limestone sulphation capacity. To evaluate this effect, iron oxide powder was added to pulverized Hat Creek ash and pelletized.

Sulphation Test Results

ASH BEDS

The sulphation capacities of Havelock limestone determined in the FBR tests with beds of ashes and sand are detailed in Table 10. With all but one ash sample, the sulphation capacity of the limestone was lower with the ash bed than with the standard silica sand bed. The Highvale ash had no apparent effect on the sulphation, while the Lingan, Coleman, Fording, and Hat Creek coal ashes slightly reduced sulphation. Most of the eastern coal ashes, Devco Prince, Evans, Minto, and Novaco caused a more significant decrease, up to about 25%, in the sulphation behaviour of the limestone.

The western (Fording, Coleman, Highvale, and Hat Creek) coal ash compositions are similar to each other, being principally SiO_2 and Al_2O_3 with 3-6% Fe_2O_3. Highvale ash, which had the least effect on the sulphation of Havelock limestone, has high calcium and sodium contents that may have captured some SO_2. Lingan has SiO_2 and Al_2O_3 contents similar to western coals but a somewhat higher iron content, 9.85% Fe_2O_3. The most obvious difference between these coals and the remaining eastern (Devco Prince, Minto, and Novaco) coals is the much higher Fe_2O_3 content, 26-44%, of their ashes, which are completely stained red with Fe_2O_3.

A semi-log graph of sulphation capacity of Havelock limestone versus Fe_2O_3 content of the ash is given in Figure 16. There appears to be an exponential decrease in sulphation with increasing iron oxide content. These observations are in agreement with those of Becker et al. who reported that Havelock limestone gave similar performance with Minto, Devco, and Evans coals (28). Because the ashes all contain high levels of iron, similar results are expected.

Table 9 - Ash sample analysis, mass per cent

| Compound	Evans	Fording	Coleman	Highvale	Mine Hat Creek	Lingan	Devco Prince	Minto	Novaco
SiO_2	27.63	70.32	60.67	52.71	59.45	58.65	40.90	38.87	44.36
Al_2O_3	11.07	17.43	28.69	23.08	30.82	22.48	17.58	14.84	21.07
Fe_2O_3	43.62	5.31	3.67	4.77	5.50	9.85	33.00	35.53	26.69
TiO_2	0.54	0.72	1.27	0.68	1.06	1.12	0.75	0.75	1.01
P_2O_5	0.88	0.56	0.25	0.43	0.01	0.10	0.41	1.62	1.26
CaO	4.61	1.67	2.41	11.93	0.96	0.54	1.73	3.59	1.24
MgO	0.86	1.42	0.88	1.31	1.16	1.54	0.80	0.52	1.00
SO_3	6.29	0.02	0.02	3.08	1.39	1.07	0.82	2.38	1.26
Na_2O	1.92	0.09	0.10	2.66	0.17	0.46	0.83	0.20	0.42
K_2O	0.94	2.17	1.31	0.35	0.76	3.98	1.50	1.64	3.00
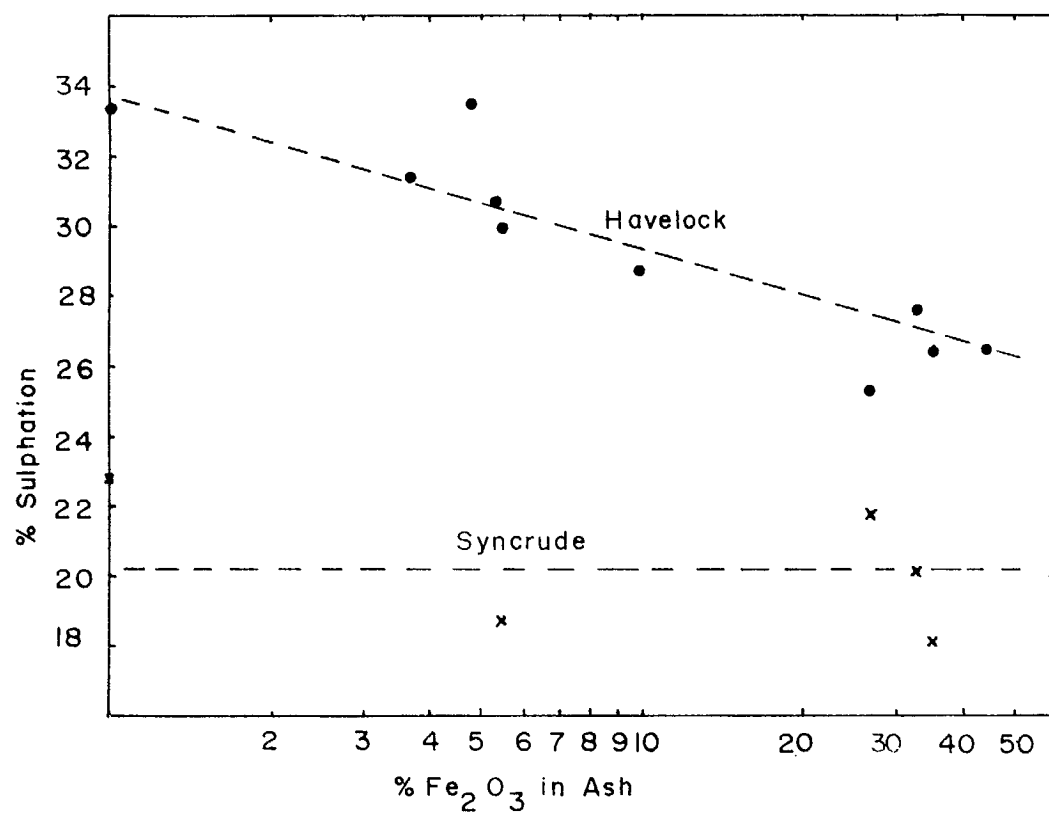
Fig. 16 - Effect of Fe_2O_3 in ash on the sulphation capacity of Havelock limestone

To determine whether ashes affected other limestones in the same manner as they did with Havelock limestone, some of the tests were run with Syncrude limestone. Unfortunately, there was an insufficient quantity of ash from the western mines to rerun all the same tests run with the Havelock limestone. The results for those ashes that were evaluated are given in Table 11 and are also shown in Figure 16. Although some decrease in sulphation is noted, the effect of the ashes is not as severe for Syncrude as for Havelock. Novaco ash, which caused the largest decrease in sulphation for Havelock, did not appear to have much effect on Syncrude limestone.

A sample of pulverized Hat Creek ash was blended with iron oxide, pelletized to produce an ash with an equivalent of 20% Fe_2O_3, and tested for sulphation capacity. The results of this test compared with those for an unadulterated ash were inconclusive, since the difference was within the limits of error for the FBR method.

PELLET TESTS

Pellets of Havelock (NB-1) and Syncrude (SY-3) limestones made with additions of reagent grade Fe_2O_3 were sulphated by the same technique as for pure limestone. The results are given in Table 12.

Contrary to the apparent negative effect of iron oxide in ash, particularly with Havelock limestone, the addition of Fe_2O_3 to pellets had essentially no effect on the sulphation capacity of either limestone. This is possibly because the finely ground limestone used in the pellets has such a large surface area compared to coarse rock, that the mass of Fe_2O_3 per area was too small to have an effect. The total mass of Fe_2O_3 in the system when incorporated with limestone pellets is about 0.5 g, whereas there may be up to 50 g of Fe_2O_3 with the ash.

EFFECT OF SO_3

Although the overall reaction for the sulphation of CaO is:

$$CaO + SO_2 + 1/2\ O_2 \rightleftharpoons CaSO_4$$
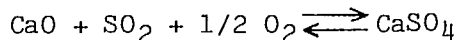
the actual reaction path is believed to be:

a) $SO_2 + 1/2\ O_2 = SO_3$ b) $CaO + SO_3 = CaSO_4$

It has been suggested that the sorbent particles are essentially transparent to the diffusion of O_2, and that the diffusion of SO_2 and perhaps formation of SO_3 are the rate-limiting steps (29). The presence of the Fe_2O_3 catalyst should increase the SO_3 concentration. Fieldes (30) and Burdett (16) contend that high concentrations of SO_3 cause a more rapid blocking of the pores in calcined lime by $CaSO_4$ than occurs with low concentrations of SO_3. Thus, reduced sulphation capacity would be expected with increased quantity of such a catalyst. This was generally observed in the present experimental results.

Table 10 - Sulphation capacities of Havelock
(NB-1-11) limestone in ash beds

Bed	X %
Silica Sand*	33.3
Evans*	26.5
Lingan	28.7
Fording*	30.7
Coleman	31.4
Highvale	33.5
Hat Creek*	29.9
Devco Prince	27.6
Minto	26.4
Novaco	25.3

*Average of two or more
tests.

Table 11 - Sulphation capacity of Syncrude
(SY-1) limestone in ash beds

Bed	X %
Silica Sand	22.8
Hat Creek	18.7
" " with 20% Fe_2O_3	21.4
Devco Prince	20.3
Minto	18.1
Novaco	21.8

Table 12 - Sulphation capacity of pellets with Fe_2O_3 addition

Limestone	Addition	Fe_2O_3 as % of $CaCO_3$	X %
NB-1	none	-	44.2
"	Fe_2O_3	5.88	44.7
SY-2	none	-	58.2
"	Fe_2O_3	1.33	58.4
"	"	6.67	59.4

However, a problem with the premise that iron oxide in the ash catalyzes the SO_2 to SO_3 and thus accelerates pore blocking, is that at 850°C and 5% O_2 there is already a significant quantity of SO_3 in the FBR. Under these conditions the equilibrium ratio of SO_3/SO_2 is 0.117. The stainless steel tube of the reactor appears to act as a catalyst for the oxidation of SO_2 to SO_3, resulting in a calculated SO_3 concentration of about 0.03%. Synthetic gas passed through a quartz tube at 850°C does not exhibit any observable formation of SO_3, as evidenced by the fact that there is no difference in the SO_2 concentration when measured by an infrared SO_2 analyzer through the tube or by-passing the tube. There is a difference with gas passing through the stainless steel reactor such that under the test conditions the flue gas with an inlet SO_2 concentration of 0.28% contains about 0.03% SO_3 in the exhaust from the reactor. This is evidenced from the graphs of SO_2 concentration in the off-gas by-pass and in the pass through the reactor (Fig. 4), which shows this 11-12% decrease in SO_2 concentration. Because the steel reactor had promoted the equilibrium SO_3/SO_2, there was no noticeable difference in this SO_2/SO_3 effect between a bed of sand or one of ash. Thus, there could not be any measureable effect of iron oxide in the ash on the SO_3 concentration. However, in a large-scale FBC lined with refractory, the high-iron ash may cause an increase in the SO_3 concentration.

Conflicting sulphation results on the effect of the addition of iron compounds to limestone were reported by Desai et al. (27), who soaked a dolomite and a limestone in $Fe(NO_3)_3$ such that the calcined rock contained 1 to 2% Fe_2O_3. They sulphated the material by TGA and reported an increase in the rate and sulphation capacity of up to 40% with the iron-catalyzed dolomite, but a decrease with the limestone. They attributed the difference to the pore-size distribution and the plugging of the smaller pores of the limestone with Fe_2O_3 during impregnation. They also pulverized the limestone, pelletized it, and coated the pellets with $Fe(NO_3)_3$. The sulphation was found to be higher for iron-treated pellets than without iron. However, the 2% Fe_2O_3 pellets were not as effective as the 1% Fe_2O_3 pellets.

Another possible explanation that may account for some decrease in sulphation with ash is suggested in a paper by Kalmanovitch et al. (31), who examined ash samples from the Summerside AFBC that contained 35 and 52% Fe_2O_3. They present evidence indicating that iron-rich ash compounds can coat the surface of a calcined lime particle and physically retard the sulphation reaction. Pomeroy et al. (32) also present evidence indicating that the sulphation of limestone particles was reduced by adherent fine particles of ash bonded to the limestone, thus reducing its active surface area.

METHODS TO IMPROVE LIMESTONE UTILIZATION

The sulphation capacity of most limestones in the 850-1000 µm size range is between 20 and 30%, with a few better and some worse. Thus, in an atmospheric bubbling fluidized-bed, where the particle size ranges from 500-3000 µm and averages about 1000 µm, approximately three-quarters of the limestone injected in the AFBC is simply calcined to CaO but does not react to $CaSO_4$, and is therefore subsequently wasted.

This bed material of ash and partially sulphated limestone can be treated to utilize the unreacted lime. One method is to pulverize the material to expose unreacted lime and to agglomerate it as pellets. Cyclone and bag house dust could also be used if the amount of unreacted material warranted it. In this manner, unburnt carbon could be recycled and the overall combustion efficiency increased (33). The pellets would be added to a second bed or unit such that the recycled material is used separately from the initial limestone.

Another approach to increasing the utilization of limestone is to hydrate the spent bed material (34). Water permeates the calcium sulphate layer and reacts with the inner calcium oxide core to form calcium hydroxide. The hydroxide, having a larger molar volume than the lime, swells and cracks the sulphate shell. Upon reinjection of this material into a fluidized bed, it dehydrates and exposes unreacted lime for further sulphation. This hydration effect also occurs with the water used in the agglomeration process.

Raw limestone utilization can be greatly improved by reducing the particle size. Unfortunately, small particles added to an AFBC will be immediately elutriated from the bed by the fluidizing air. Agglomeration of the fine particles into pellets overcomes this problem. Pelletizing also offers the opportunity to incorporate salts with the sorbent to further improve sulphation capacity.

The following section describes the pelletization and sulphation testing of sorbents previously evaluated as natural rock. Some work is described on the reuse of sulphated bed material from the Summerside AFBC.

EXPERIMENTAL PROCEDURE

Pelletization

The limestone and dolomite samples were prepared by crushing, grinding, and sieving. The -149 μm (-100 mesh) size fraction from these operations was the feedstock for the pellets. The actual size distribution of this fraction varied from sample to sample, being dependent to some extent on the hardness of the rock. No attempt was made to adjust the size distribution below 149 μm. Table 13 gives the particle size distribution for several samples as determined with a Leeds and Northrup Microparticle Analyzer. The mass weighted average particle diameter of limestone samples is computed from the following relation:

$$dp = \frac{1}{\sum_i (x/dp)i}$$

Dp ranged from 25 to 81 μm. Dolomite samples were noticeably coarser, being in the order of 80 μm.

A 40 cm diameter (16 inch) disc pelletizer was used to produce all the pellets. A very fine spray of water for binding pellets blended with bentonite, or sodium carbonate solution, was achieved with an air-pressurized container and an atomizer nozzle. A vibratory feeder was used to regulate the limestone feed to the rotating disc.

For the bench-scale reactor tests, fairly small pellets were desired, 850-1000 μm, since this is the standard particle size used in the sulphation evaluation. The disc pelletizer produced a variety of sizes approximately 5 mm and smaller. These large pellets that formed were crushed by hand during the operation. Normally 0.5-1.0 kg was pelletized for each limestone sample and at the completion of material feeding, the pellets were allowed to roll on the disc for a further 10 min to improve their compaction. The moisture content of the green pellets was measured on a moisture determination balance. Moisture was found to range between 10% and 14%. Pellets were oven dried at 85°C overnight and then sieved to provide the sized material for sulphation testing. Occasionally, when there was an insufficient quantity of 850-1000 μm pellets, larger pellets were crushed in a disc pulverizer and sieved to provide broken pellets in the desired size range.

Several types and amounts of binders were used in this test series. The most commonly used dry binder was bentonite, although portland cement, quick-set cement, and plaster of paris were also tried. In each case, the binder was blended with the limestone prior to pelletizing. Sodium carbonate solution was also used as a binder and was sprayed as a fine mist onto the limestone as it was fed to the disc.

Three samples of spent bed material from the Summerside AFBC unit were pulverized and pelletized. The samples were not fresh and had partially hydrolyzed such that by itself the material made fairly weak pellets. Stronger pellets were obtained when 2% bentonite or 5% $NaCO_3$ solution was added as a binder.

Pellet Tests

After making the pellets on the disc, green pellets were subjected to a drop test from about 45 cm onto a steel plate or the floor. Good pellets would survive several drops before breaking. After drying, the pellets were tested for compressive strength in an Allis Chalmers Pelletester. Ten samples, in a sieved size range of 3360-4760 μm, were tested for each batch of pellets. The resistance to thermal shock and abrasion were qualitatively evaluated by observing the quantity of dust collected in the cyclone during a sulphation test run. Normally this quantity was very small and, as it could be contaminated with some fine silica sand bed material, it was not weighed.

Hydration

In a preliminary experiment on hydration enhancement of sorbents, a half dozen samples of 850-1000 μm limestone were sulphated in the fluidized-bed reactor. This material was separated from the sand bed by sieving, the sand being slightly finer than the limestone. The sulphated limestone was then allowed to soak in water at room temperature for approximately one day, after which it was placed in a 95°C oven until all the unreacted water was evaporated. The hydrated samples were reinjected into the reactor and sulphated until the emission curve indicated that the reaction was complete. The bed material was again separated from the sand bed by sieving and submitted for chemical analysis to determine the overall sulphation conversion.

In a second experiment 30 g samples of limestone were sulphated, sampled for analysis, then the remainder was hydrated, dried, re-sulphated, and analyzed.

TEST RESULTS

Pellet Characteristics

The essential criterion of pellet quality is the ability to survive handling, storage, and use in a fluidized-bed combustor. These are reflected in the pellet strength, abrasion resistance, and resistance to thermal shock (35). Ten pellets per sample were tested in the Pelletester. There was a considerable variation in the values obtained. Neither plaster of paris nor Portland cement produced pellets of sufficient strength to warrant further testing. Although Quick-set cement produced strong pellets, material costs in the order of $50/t pellets were considered too high for this binder to be of practical use. The quantity of bentonite was experimentally found to be optimum at about 2% with NB-1 limestone. Increasing the binder content above this did not appreciably increase the pellet strength. The optimum quantity of binder would probably vary with the limestone source and particle size. The average crushing strength of pellets bound with bentonite in the 3600-4760 μm size range was 2.0 N.

Two sodium carbonate solution concentrations were tested as binders: a 5% solution and a saturated solution that was approximately 10%. The pellets made with the more concentrated solution were stronger; however, as the 5% Na_2CO_3 solution produced pellets of satisfactory strength, this concentration was used for the tests. The crushing strength averaged 3.4 N. On a dry basis, the concentration of Na_2CO_3 in the pellet was approximately 1.3%.

No specific test was devised or used to measure attrition or decrepitation due to thermal shock. An indication of the breakdown of pellets in the fluidized bed is given by the quantity of cyclone dust collected. In no case was the quantity of dust considered excessive. During sulphation in the fluidized-bed, the formation of calcium sulphate at the surface of the pellet actually increases its strength and subsequent resistance to attrition.

Sulphation Capacity

Table 14 gives a comparison of the sulphation capacity of the natural rock and of pellets made with bentonite and with sodium carbonate binders. The improvement in the sulphation capacity of the pellets compared with the natural rock is quite dramatic, the increase being from two- to fivefold. In fact, all of the pelletized rocks would be classified as excellent sorbents for SO_2 in AFBC.

The sulphation capacity of the pelletized material does not appear to bear any relationship to the capacity as coarse limestone. For example, the Havelock limestone (NB-1), which is a good sorbent, increases from 33% as rock to 39% as pellets bound with bentonite and up to 61% as pellets bound with sodium carbonate. Brookfield limestone (NS-4 and 8), which is totally unacceptable as a sorbent in coarse sizes (16-18% capacity), is an excellent sorbent (65+%) when finely ground and pelletized with either binder.

Table 13 - Particle size distribution of carbonate rocks, µm

Size µm	NB-3	NS-5	NS-7	NB-4	NS-9
176	16.8	2.4	1.5	0.0	6.0
125	26.2	11.6	10.4	7.2	14.7
88	21.9	9.8	11.5	8.5	14.0
62	13.1	9.7	12.1	5.2	13.4
44	5.6	7.5	10.9	7.3	4.2
3.1	3.7	5.4	9.9	8.5	5.0
22	5.5	10.2	9.4	8.3	5.5
16	0.0	8.9	7.5	9.2	7.4
11	3.0	8.1	7.4	11.2	4.5
7.8	0.0	7.0	6.1	9.0	3.4
5.5	0.4	6.1	4.0	8.3	8.0
3.9	3.4	5.6	3.0	7.1	6.3
2.8	0.0	7.1	5.6	9.6	7.0
Mass weighted average particle diameter, µm					
	81.0	37.8	39.5	27.1	48.7

Table 14 - Sorbent sulphation capacity of carbonate rocks and pellets, 850-1000 µm material

Sample	Rock	Average diam µm	Pellets 2% ben	Pellets 5% Na_2CO_3
NS-1 Irish Cove	27.2	51	44.1	-
-9 " "	25.1	49	39.4	62.7
-2 Kelly Cove	18.4	-	40.5	40.5
-4 Brookfield	16.0	-	63.3	73.4
-8 "	17.7	34	66.1	69.4
-5 Calpo	34.0	38	58.2	66.5
-6 Glencoe	23.2	53	43.6	39.9
-7 "	21.9	39	36.7	50.7
-11 "	21.2	-	37.9	-
NB-1 Havelock	33.1	34	39.4	60.7
-2 Carlisle	25.4	-	-	63.7
-3 Brookville	26.7	81	-	63.0
-4 Elmtree	19.1	27	44.0	63.5
-5 Windsor	25.9	-	45.3	67.1
GR Gays River	-	-	85.6	95.9
SY-2 Syncrude	24.1	-	63.6	-
CS-1 Clarson	26.2	-	-	62.7
ALT-7 Exshaw	20.0	15	52.3	-
ALT-6 Suncor	26.24	-	67.5	-
ALT-7 Cadomin	22.3	-	61.1	-

The material pelletized with sodium carbonate binder tends to have higher sul-
phation capacities than those with bentonite. In some samples, the improve-
ment with sodium carbonate binder is more than 50% greater than with bentonite.
Part of the difference may be attributable to the difference in strength or
abrasion resistance of the two binders, sodium carbonate being the stronger
and presumably more resistant to loss of material due to attrition. The alka-
li itself may be beneficial as evidenced by the work at Argonne National Labo-
ratory where sodium carbonate addition to limestone improved performance (36,
37). They postulate that when salt-treated limestone is heated above 700°C,
trace amounts of liquid form that increase the mobility of ions in the CaO
matrix. The higher mobility via surficial liquid films enhances crystalliza-
tion of CaO and $CaSO_4$, resulting in the formation of large pores, with their
enhanced sulphation capacity, at the expense of small ones.

The equations of the sulphation curves for pellets with bentonite and sodium
carbonate binders are given in Tables 15 and 16. This data will be used later
in modelling.

Effect of Particle Size

Other than screening through a 149 μm (100 mesh) sieve, no attempt was made
to size the material used to make pellets. As can be seen from Tables 13 and
14, there is an appreciable variation in the average particle size and size
distribution of the ground material. These variations reflect the differences
in the physical nature of the limestones. To evaluate the effect of material
particle size, two dolomites, NS-2 and NB-3, were ground in a disc pulverizer,
a portion was removed for pelletizing, and the remainder was ground a second
time. Figure 17 shows that for pellets of this material there is a consider-
able improvement in sulphation with the reduced particle size. The finer
material was easier to pelletize and produced stronger pellets than the coars-
er size. Being stronger there will be less loss due to attrition, which could
account in part for the higher sulphation capacity. It is probable that there
is an economically optimum size to which a limestone should be ground, since
grinding costs increase with decreasing particle size. In a large-scale
operation, size reduction of the limestone would be accomplished with jaw,
cone, or gyratory crushers followed by perhaps a hammermill and then a ball
mill. The size distribution of the limestone would no doubt be different than
in these tests. Therefore, these sulphation capacity results should be con-
sidered as indicative of expected performance of finely ground material rather
than as absolute values.

Effect of Pellet Size

Sulphation tests were conducted on pellets sieved at 850-1000 μm since this
is the standard size for this procedure. To determine whether pellet size had
an effect on sulphation, a series was run with Gays River tailings pellets and
also with Glencoe (NS-6) pellets. The results, given in Table 17, somewhat
surprisingly showed that the largest pellets gave the highest results. A
probable explanation for these results is that the smaller pellets are weaker,
and more susceptible to attrition and subsequent loss of material. It would
appear that the larger pellets are sufficiently porous such that increasing
size does not offer resistance to sulphation. That is, the sulphation reac-
tion is essentially independent of pellet size.

Table 15 – Sulphation parameters of pellets with 2% bentonite binder

Sample	X %	a	k	n
NS-1	44.1	44.06	0.03422	1.1141
NS-9	39.4	39.48	0.04307	1.1104
NS-4	63.3	63.66	0.02497	1.1832
NS-8	66.1	65.59	0.02431	1.1513
NS-5	56.6	58.22	0.02476	1.1362
NS-6	43.6	43.54	0.04386	1.0813
NS-7	36.7	36.89	0.04403	1.1345
NS-11	37.0	36.96	0.04260	1.1745
GR	83.7	85.62	0.07645	0.7310
NB-1	39.4	39.57	0.04752	1.1464
NB-3	30.4	30.87	0.08516	1.2338
NB-4	44.0	43.16	0.03922	1.1624
NB-5	45.3	45.29	0.03239	1.1776
SY-2	57.7	56.90	0.04340	0.8463
ALT-4	52.3	53.57	0.03424	1.0331
ALT-5	59.2	61.15	0.02464	1.0889
ALT-6	67.5	66.73	0.0364	1.0810
ALT-7	61.1	61.88	0.0314	1.0220

Table 16 – Sulphation parameters of pellets with 5% Na_2CO_3 binder

| Sample	X %	a	k	n
NS-2	40.5	40.08	0.13058	0.9553
NS-4	73.4	77.14	0.02434	1.1261
NS-8	69.4	71.748	0.02074	1.236
NS-5	66.5	66.81	0.03386	1.1936
NS-6	39.9	40.00	0.06410	1.1978
NS-7	50.8	51.36	0.02736	1.3108
NS-9	62.7	64.01	0.02683	1.0993
NB-1	60.7	62.26	0.02456	1.1997
NB-2	59.0	59.017	0.02828	1.1645
NB-3	63.0	62.19	0.07048	1.0233
NB-4	67.3	68.87	0.02170	1.2031
NB-5	72.5	72.26	0.02183	1.1806
GR	94.5	95.93	0.04015	1.0914
CS-1	62.7	65.98	0.02831	1.1142
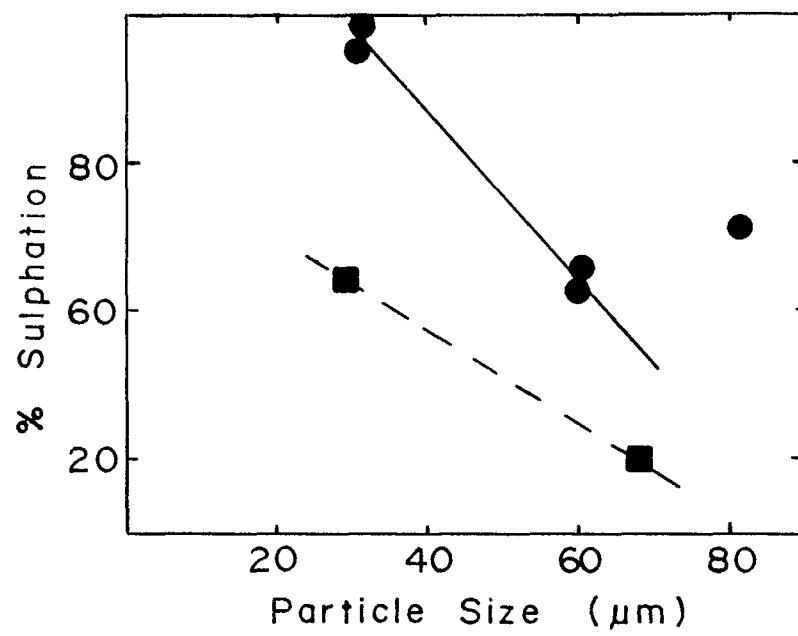
Fig. 17 - Effect of particle size on the sulphation of dolomite pellets

Hydration of Sulphated Limestone

The results of the preliminary hydration enhancement experiments, given in Table 18, are very encouraging. The samples were sulphated, hydrated, and sulphated a second time. The degree of the initial sulphation was not measured, nor was the extent of hydration. The sulphation capacities are calculated from the chemical analysis of calcium and sulphur in the resulphated bed material. For comparison purposes, the previously determined sulphation capacities of the untreated limestones are also given. All hydrated samples indicate a substantial increase in sulphation capacity, NS-6 showing more than three times the initial capacity.

A 30 g sample of NB-1 was sulphated, the sulphation capacity being calculated as 37%. Chemical analysis of the bed material for Ca and S resulted in a sulphation conversion of 40.5%. It should be noted that the chemical analysis of the bed material generally results in slightly higher sulphation than that calculated from the emission curves. Part of the difference may be attributable to attrition and dust loss of unreacted material, which would result in lower sulphation capacity for the FBR method.

The sulphated sample of NB-1 was placed in water for 24 h and then allowed to air dry for three days. A portion of this hydrated material when heated to 625°C gave a weight loss of 11.2%, which was assumed to be the water content. Calculations indicate that if all of this weight loss were water of hydration, the unsulphated lime was hydrated to 88%. The hydrated sample was resulphated and the bed material was analyzed. From the sulphation curves, the overall sulphation was calculated as 59%. The chemical analysis of the bed material gave 70% conversion.

A potential problem with the hydration method of improving sulphation capacity is in the physical nature of the hydrated limestone. As noted previously, when water reacts with the CaO to form $Ca(OH)_2$ the particle swells and cracks (34). If the sample is resulphated soon after hydrating, the method works very well. However, if there is a time delay of weeks before the material is reused, the hydration reaction appears to continue and the particle becomes very soft and powdery. This effect may even be observed with sulphated bed material that has been stored in an open container and allowed to absorb moisture from the air. Reinjection of this type of "over-reacted" material into the AFBC would result in excessive attrition and loss of material by elutriation.

Sulphated-Bed Material

Several samples of bed material, SA-1, SA-2, and SA-3, composed of ash and partially sulphated lime, were obtained from the start-up operation of the Summerside AFBC. One sample, SA-4, was from CCRL and was diluted with sand. In all cases the initial feed was Havelock limestone. The calcium analysis of the Summerside AFBC bed material indicates that it contains less than 30% ash, the remainder being sulphated limestone. The samples were tested in the FBR after fine grinding and pelletizing with bentonite and sodium carbonate. The results are given in Table 19. The initial degree of sulphation was determined by chemical analysis on the pellets and is given as mol % S/Ca. The sulphation of the remaining unreacted calcium is given as X %. The overall sulphation is the combination of the two.

Table 17 - Sulphation capacity versus pellet size

	Sieve size, μm		
Sample	850-1000	600-850	300-600
Gay's River	94.5	80.7	78.5
Glenco	43.8	44.9	39.2

Table 18 - Hydration enhancement of sulphation capacity

Limestone	Rock % sulphation	Hydrated sample % sulphation
NS-5	34.0	50.8
NS-6	23.3	69.2
NS-7	21.9	53.3
NS-9	25.1	64.7
NS-11	21.2	45.5
NB-1	33.1	59.9

Table 19 - Sulphation capacity of pelletized spent bed material

	Chemical analysis					Total
Sample	% Ca	% S	mol % S/Ca	Binder	X %	sulphation
SA-1	39.27	8.55	27.2	2% ben	37.7	64.9
SA-1				5% Na_2CO_3	41.5	68.7
SA-2	35.38	9.07	32.0	2% ben	42.5	74.5
SA-2				5% Na_2CO_3	50.1	82.1
SA-3	45.52	10.63	29.2	5% Na_2CO_3	23.7	52.9
SA-4	15.38	2.56	20.8	5% Na_2CO_3	60.2	81.0

With the exception of SA-3, the sulphation capacity of the lime in the re-
cycled material exceeded that of the unreacted limestone. That is, the over-
all sulphation was more than twice that of the once-through limestone. Sodium
carbonate was the preferred binder, although if fresh material had been avail-
able, it is unlikely that any binder would have been required. Although these
tests used only bed material, cyclone and bag house dust could also be incor-
porated as pellets. This has the added advantage of recycling unreacted
carbon to the combustor. Pellets of partially sulphated lime would be used
in a different combustion stage or bed to that for fresh limestone in order
to separate the two.

MODELLING TO PREDICT SORBENT PERFORMANCE

There are a multitude of models for predicting the performance of limestone
as SO_2 sorbents during the combustion of coal in AFBC (7,8,38-41). Normally,
models utilize data from laboratory test facilities such as TGA or small
fluidized-bed test rigs and attempt to predict the behaviour of sorbents. The
mathematics of models can be very complex and the calculations present an
onerous task unless computers are used. The real test of any model is, of
course, whether it can accurately predict limestone requirements versus
SO_2 retention for large-scale AFBC units. Unfortunately, there are few such
units in operation and most comparisons are made against small-scale pilot
AFBC's. Often the scatter in the AFBC data is so great that any number of
model prediction curves could be considered an acceptable fit.

One of the most comprehensive modelling studies has been conducted by the
Argonne National Laboratory. Reference 7 is a text of more than 400 pages of
detailed description of their model and numerous examples of sorbents modelled
with TGA data. A number of simple calculations that incorporate the physical
characteristics of the sorbent and also of the AFBC unit being modelled are
required to determine the various parameters used in the model. The sulpha-
tion data can be used graphically to determine the reaction rate and the maxi-
mum utilization parameter as described in the above reference. Alternatively,
the sulphation curve equation can be incorporated in a computer program using
Laguerre polynominals to solve a numerical integration. This program was
acquired from Dr. Johnson. His description of the Argonne model for SO_2
capture in AFBC and of the computer program are given as Appendices A and B.
The author has written a program, which incorporates Dr. Johnson's program,
to perform the calculations required by the model. This is given as Appendix
C.

Modelling CCRL's AFBC

A series of combustion trials with three sizes of Havelock limestone and three
superficial velocities was conducted with Devco Prince coal in the CCRL pilot-
scale AFBC (42). A second test series was made with two of the three previ-
ously used sizes of limestone and Evan's coal (43). Each test with a specific
particle size and velocity was conducted with and without recycle of fines
back to the bed. The fluidized-bed operating conditions and other parameters
necessary for the model are given in Table 20. Three sulphation curve equa-
tion parameters are given: the Havelock limestone in a sand bed, and in beds
of Evans and Devco Prince coal ash.

Table 20 - CCRL pilot AFBC operating parameters
and sorbent characteristics

Temperature	850°C
Pressure	101 kPa (1 atm)
Fluidizing velocity	1.22, 2.13, 3.05 m/s
Static bed height	0.46 m
Expanded bed height	0.66 m
Area of bed	0.155 sq. m
Distributor openings	400
Coal feed rate	Variable from 22 to 58 kg/h
Sulphur content	Variable from 2.9 to 6.8%
Sorbent	Havelock Limestone
Calcium content	95% $CaCO_3$
Sorbent particle size	6*20 mesh (avg. 1.213 mm), 1/4"*0 (avg. 1.593 mm), 1/4"*20 mesh (avg. 2.404 mm)
Sorbent bulk density	1.45 g/cc
Sorbent particle density	2.53 g/cc
Sulphation curve eqn	sand bed: a = 33.0, k = 0.0563, n = 0.8384
Sulphation curve eqn	Evans ash: a = 24.9, k = 0.1229, n = 0.7213
Sulphation curve eqn	Devco ash: a = 27.9, k = 0.1043, n = 0.7103
Test particle size	18*20 mesh (avg. 0.925 mm)
Test SO_2 concentration	2700 ppm

Table 21 - Summerside AFBC operating parameters

Temperature	850°C
Pressure	101 kPa
Fluidizing velocity	1.83 m/s
Static bed height	0.6 m
Expanded bed height	1.5 m
Area of bed	3.52 sq. m (A bed), 3.96 sq. m (B bed)
Distributor openings	284 (A bed), 472 (B bed)
Coal feed rate	1500 kg/h
Sulphur content	4.0%
Sorbent	Havelock limestone
Sorbent particle size	8*20 mesh (avg. 1.24 mm)

Figures 18 to 20 show the actual SO_2 retention versus the Ca/S mole ratio
for the pilot AFBC tests with three sorbent sizes and two coals. Three model
prediction curves are plotted: one from the FBR data for this limestone in a
sand bed, and the others in the Evans and Devco ash beds. There is a fair
amount of scatter in the data so that, in all cases, the curves based upon the
model prediction are in reasonable agreement with the data. In general, the
model curves based upon the limestone in the sand bed test data tend to over-
predict the SO_2 capture for the tests with no ash recycle and to under-predict
it for the tests with recycle. The two ash bed curves are fairly close to-
gether. They are in good agreement with the data for the CCRL tests with no
recycle, but over-predict sorbent requirements when the ash is recycled.

There is less data scatter in the tests with the 850-2380 µm limestone
(Fig. 18), perhaps because it has the narrowest size range of the three size
ranges tested. The average particle size in that test series, 1210 µm, is
closest to that used in the FBR test, 925 µm. The -6300 µm size (Fig. 19)
has the widest size distribution and includes more fines than the other test
sizes, and the data show a wider scatter than Figure 18. Figure 20 showing
the 850-6300 µm limestone size was only tested with one coal. This test had
the largest average particle size. Both the model and the test data indicate
that the fluidizing velocity, within the range tested, has very little effect
on SO_2 retention. Sorbent particle size appears to be the parameter with the
greatest effect on sulphur capture.

Modelling Summerside AFBC

Since the Summerside AFBC is the largest in operation in Canada, it was chosen
as the unit to model for comparison of the limestones and dolomites. The
physical and operating parameters of the AFBC are given in Table 21. The sor-
bent parameters are the same as those listed in Table 20. More detailed des-
criptions of the Summerside AFBC are given in reference 9.

The predicted performance of Havelock limestone, which is used for SO_2 con-
trol in the Summerside AFBC, is shown in Figure 21. The curve is based on FBR
data in a sand bed. Plotted on the graph are data on SO_2 retention for the
combustion trials of three coals: Devco Prince, Brogan, and Evans, at 65% MCR
(manufacturers certified boiler rating) and 100% MCR. The predicted perform-
ance is in good agreement with most of the operational results. The perform-
ance of Havelock and the six other New Brunswick sorbents that might have been
used in the Summerside AFBC are shown by curves of Ca/S mol ratio versus % SO_2
retention in Figure 22. This graph indicates that the Havelock (NB-1) is the
best limestone for capturing up to 90% SO_2. On a Ca/S basis, Brookville
(NB-3) and Glebe Mine (NB-6) are the next best. However, Brookville is a
dolomite and on a basis of the mass of sorbent required per kg of 4% S coal,
the performance rating changes and the dolomite becomes the least efficient
sorbent. The set of curves for the quantity of sorbent required is shown in
Figure 23.

The predicted performance of Cape Breton Island and mainland Nova Scotia lime-
stones, if they were to be used in the Summerside AFBC, are shown in Fig-
ures 24-27. The best limestone is Calpo (NS-10). However, the performance
of limestone from this source is sample dependent as evidenced by the poorer
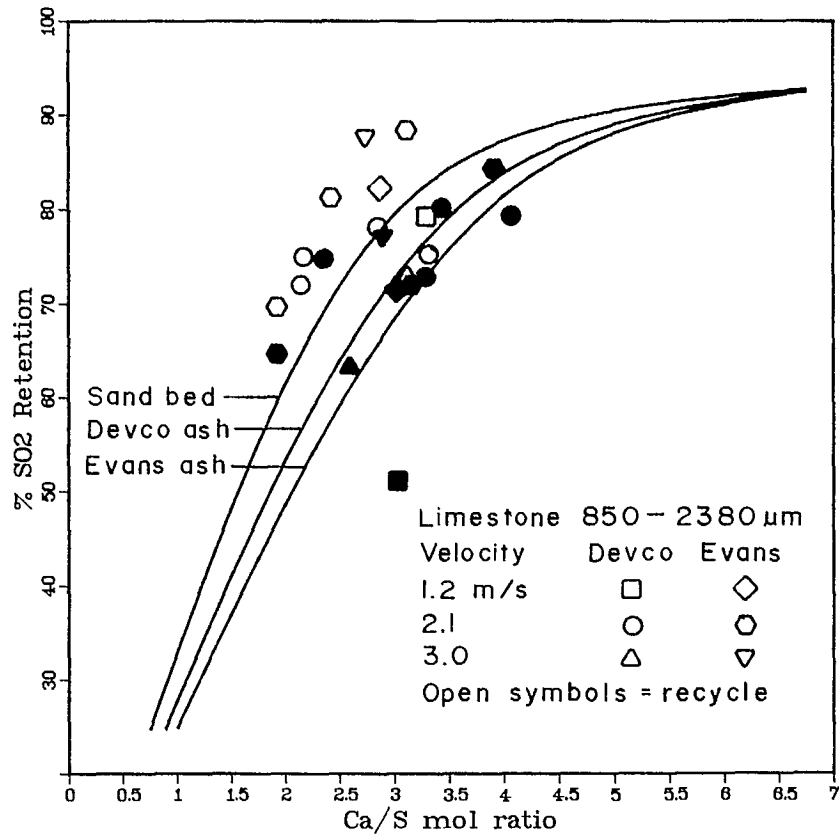results, although still very good, of NS-5 collected eight months earlier.

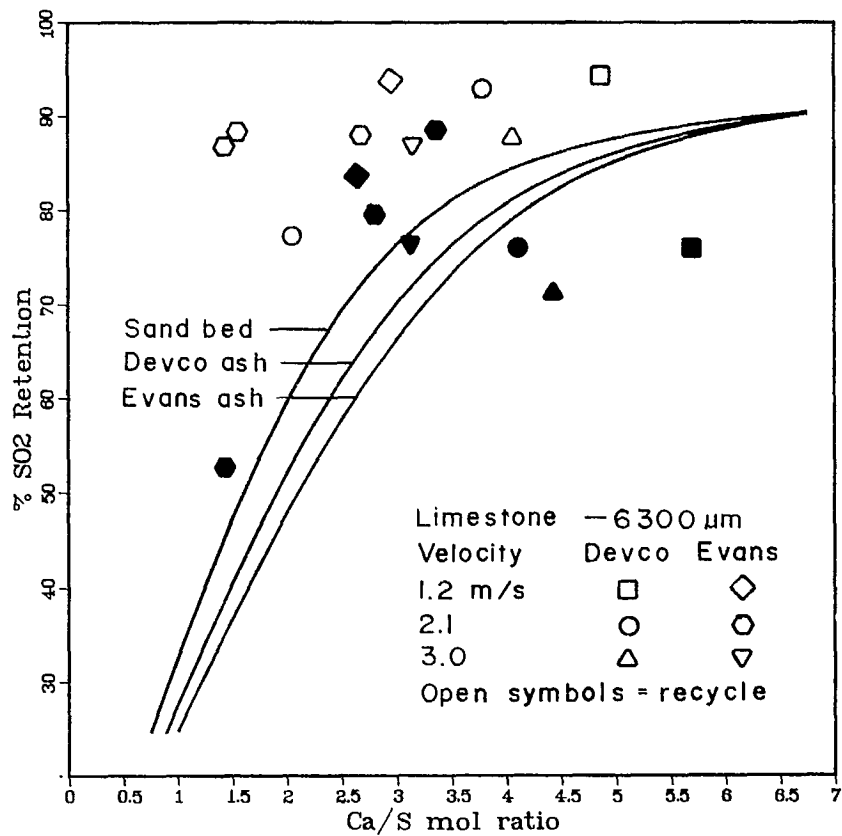Fig. 18 - Performance of Havelock limestone, 850-2380 μm in the CCRL FBC

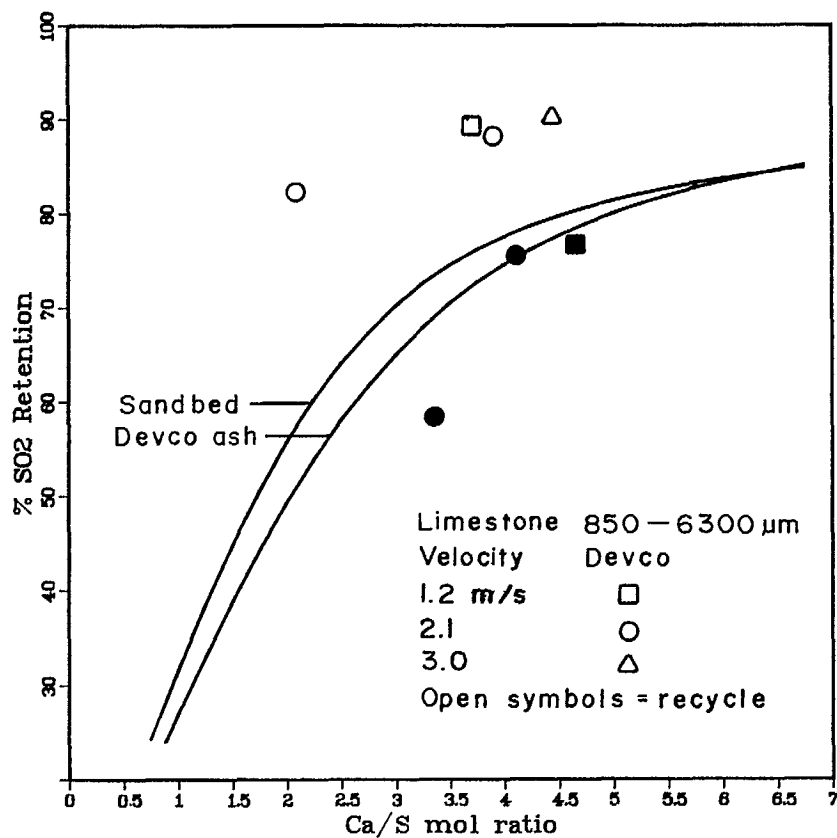Fig. 19 - Performance of Havelock limestone, -6300 μm in the CCRL FBC

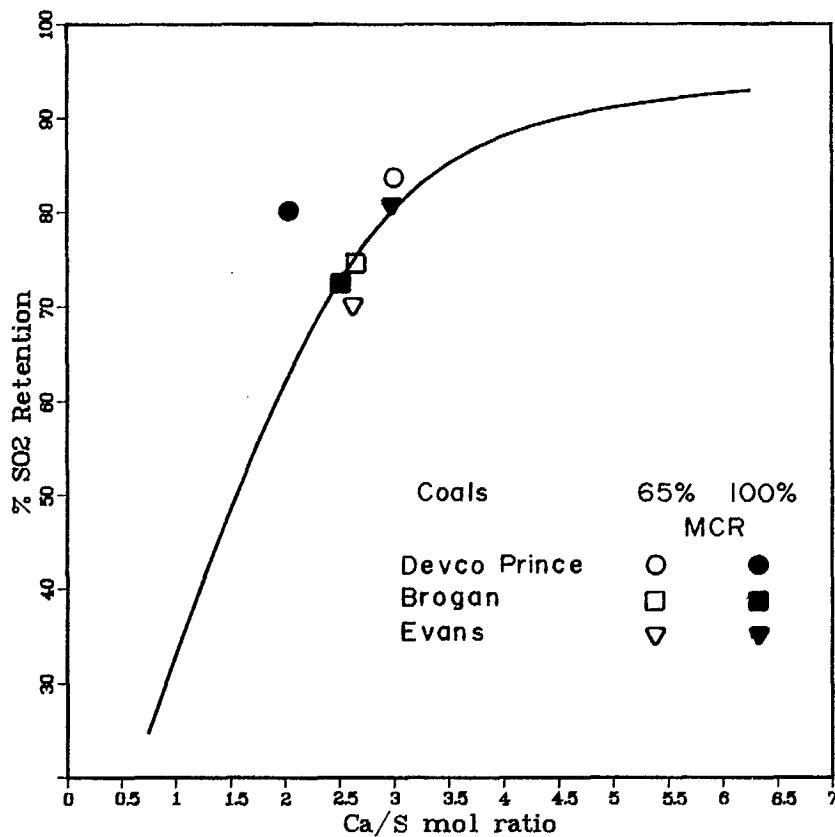Fig. 20 – Performance of Havelock limestone, 850-6300 μm in the CCRL FBC

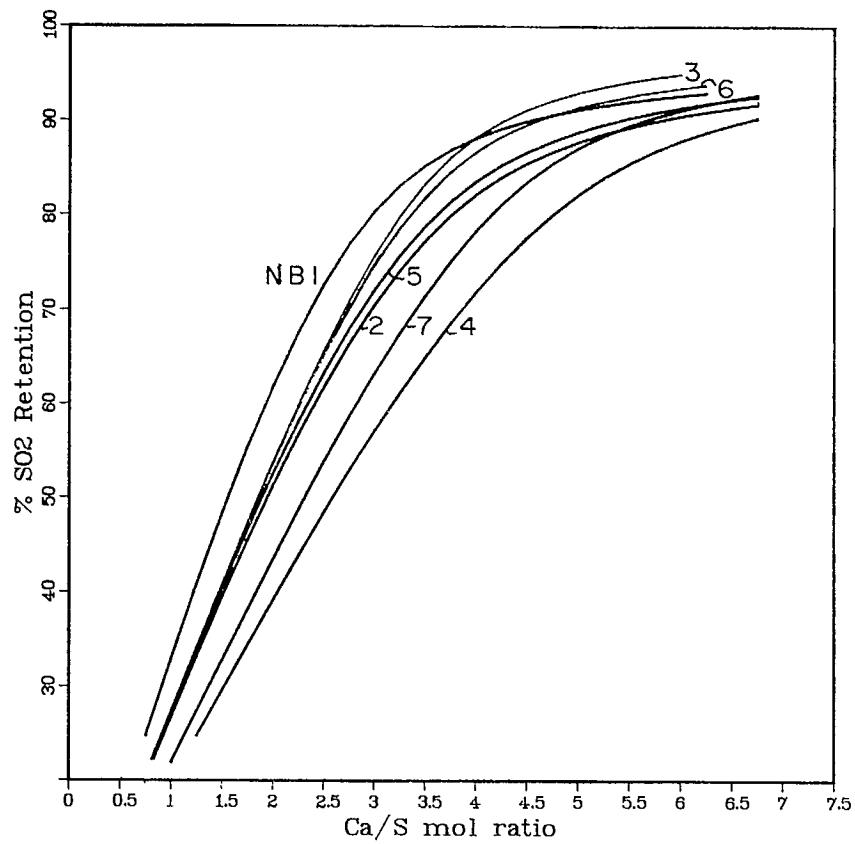Fig. 21 – Performance of Havelock limestone, 850-3360 μm in the Summerside FBC

Fig. 22 - Predicted performance of New Brunswick sorbents in the Summerside FBC
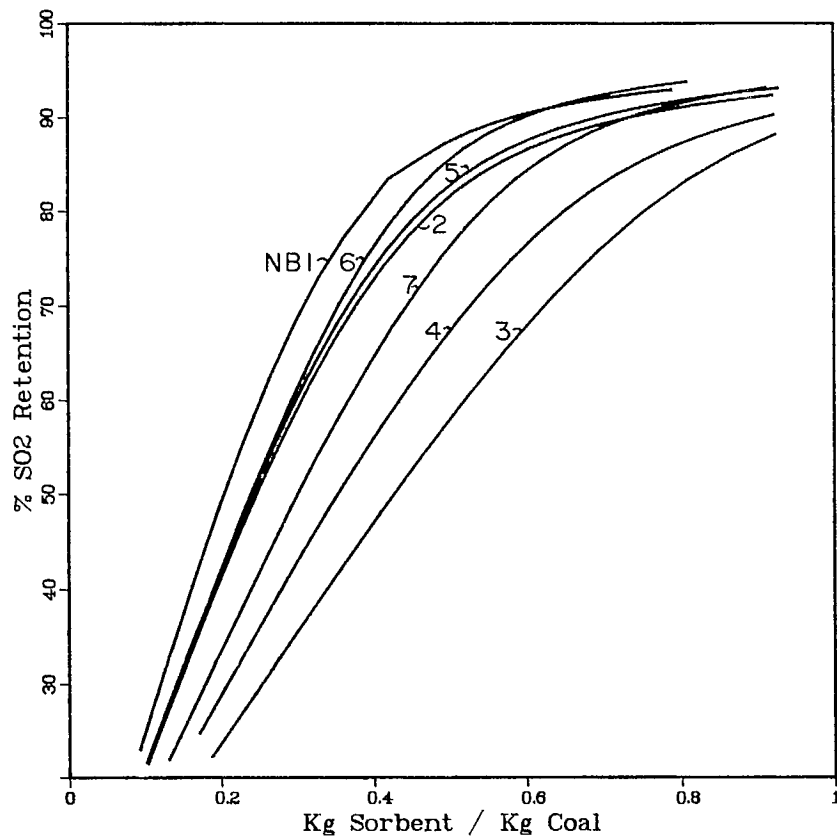

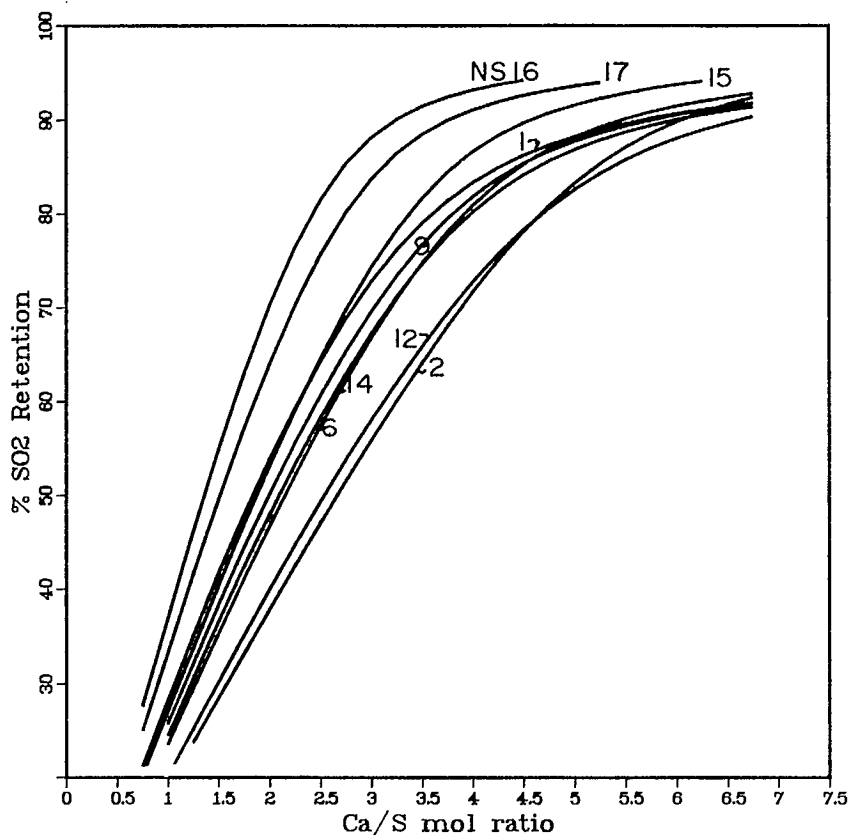Fig. 23 - Predicted quantity of New Brunswick sorbent required for the Summerside FBC combusting 4% S coal

Fig. 24 - Predicted performance of Cape Breton Island, Nova Scotia sorbents
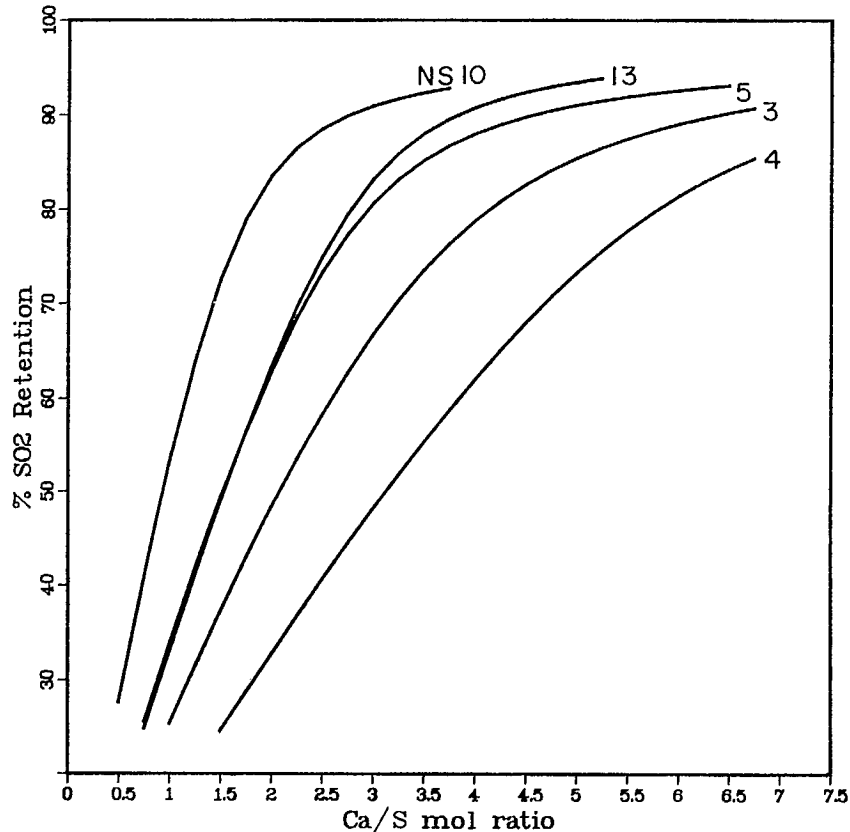in the Summerside FBC

Fig. 25 - Predicted performance of mainland Nova Scotia sorbents in the
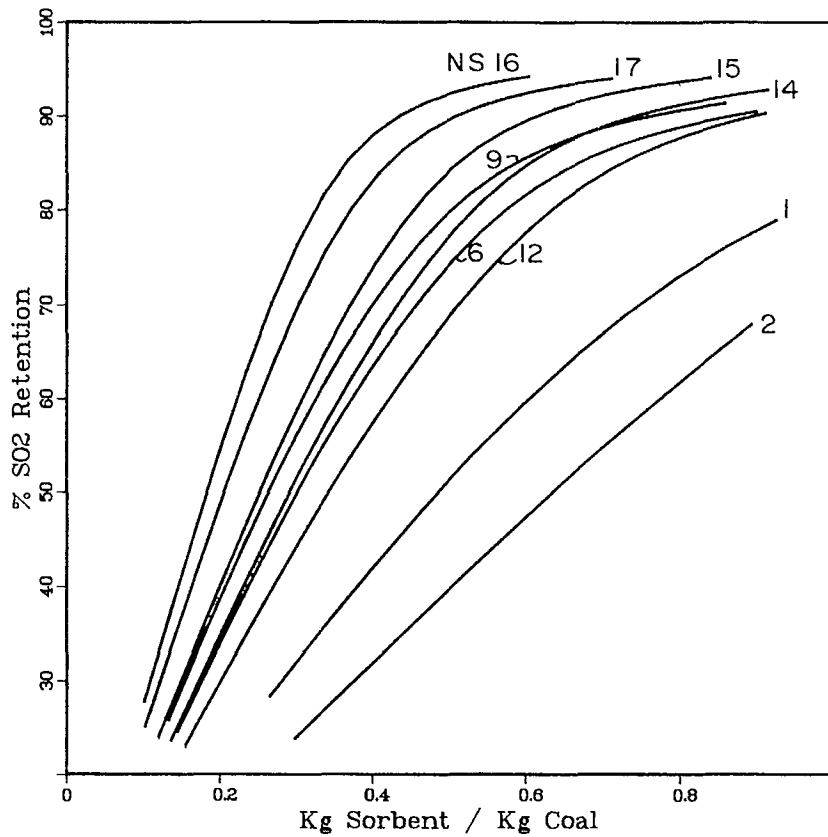Summerside FBC

Fig. 26 - Predicted quantity of Cape Breton Island, Nova Scotia sorbents required for the Summerside FBC combusting 4% S coal
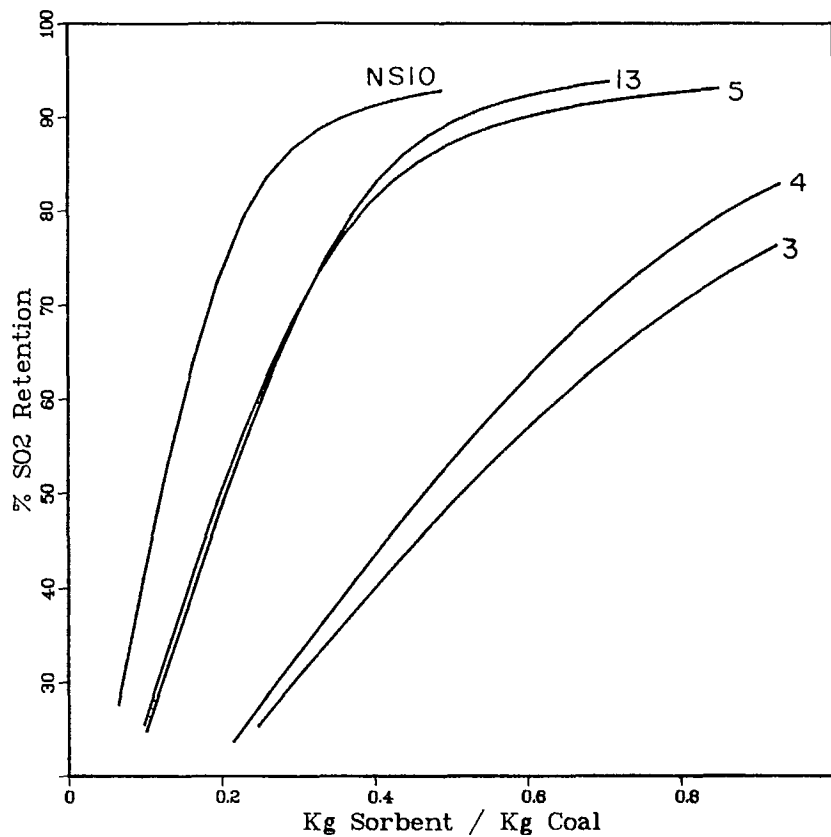

Fig. 27 - Predicted quantity of mainland Nova Scotia sorbent required for the Summerside FBC combusting 4% S coal

Another very good deposit is East Bay (NS-15 and 16), although here again there is considerable difference between the two samples taken 1 km apart. Gabarus Lake (NS-17) is another very good Cape Breton limestone. The lime-stone sample from the Upper Musquodobit (NS-13) is also very good. The dolomite (NS-3) from the same source is a poor sorbent when considered on a mass basis. The Irish Cove samples (NS-1 and 9), although taken at different times, behave in a similar manner. Only the highest and the lowest of the four Glencoe samples are plotted (NS-6 and 12). The Brookfield quarry samples (NS-4) and the Kelly Cove deposit (NS-2) are the poorest performers of the samples tested from this province.

The Alberta limestone's predicted performance is shown in Figures 28 and 29. There is less spread in the sulphur capture capacity within this series of limestones than for those from the other provinces. All are fair performers.

Model Predictions for Pelletized Limestones

The sulphation curve parameters for some pelletized limestones are given in Tables 15 and 16, and some graphs using this data are given in Figures 30 to 32, which show the predicted performance of these pellets in the Summerside AFBC. Also included for comparison in the graphs are repeat tests of the curves for some of the 850-1000 μm limestones. The predicted performance of pelletized sorbents is quite dramatic, the quantity of sorbent required to achieve 80-90% SO_2 capture being a factor of at least two, and occasionally up to five times less than that required for the coarse limestone. Some very poor sorbents, as rock, perform better as pellets than pellets of good lime-stones. Thus, the Brookfield limestones (NS-4 and 8), which are among the worst sorbents as natural rock, perform slightly better than Calpo limestone pellets (NS-5 and 10), which are the best natural sorbents. For most pellets bound with sodium carbonate, 90% SO_2 retention is possible with a Ca/S ratio of 2.0-2.5. It is important to remember that the results of pellet tests depend upon particle size, and the pellet's resistance to attrition and mate-rial loss. The results of the modelling analysis should be taken as indica-tive of sorbent behaviour rather than absolute values.

Limitations of the Model

As shown above, the model is useful in determining the relative ranking of a series of sorbents. In the CCRL tests and the few data points from the Summerside AFBC, the model gave a reasonable indication of the expected per-formance of a sorbent. There are, however, certain caveats associated with the use of the model. In the fluidized-bed reactor method, sulphation curves are obtained with a standard particle size of 850-1000 μm. It is assumed that this size represents the average behaviour of all the particles in the fluidized bed. If the particle size distribution in the bed is not too wide, and if the average size is reasonably close to that of the test, then the assumption is valid.
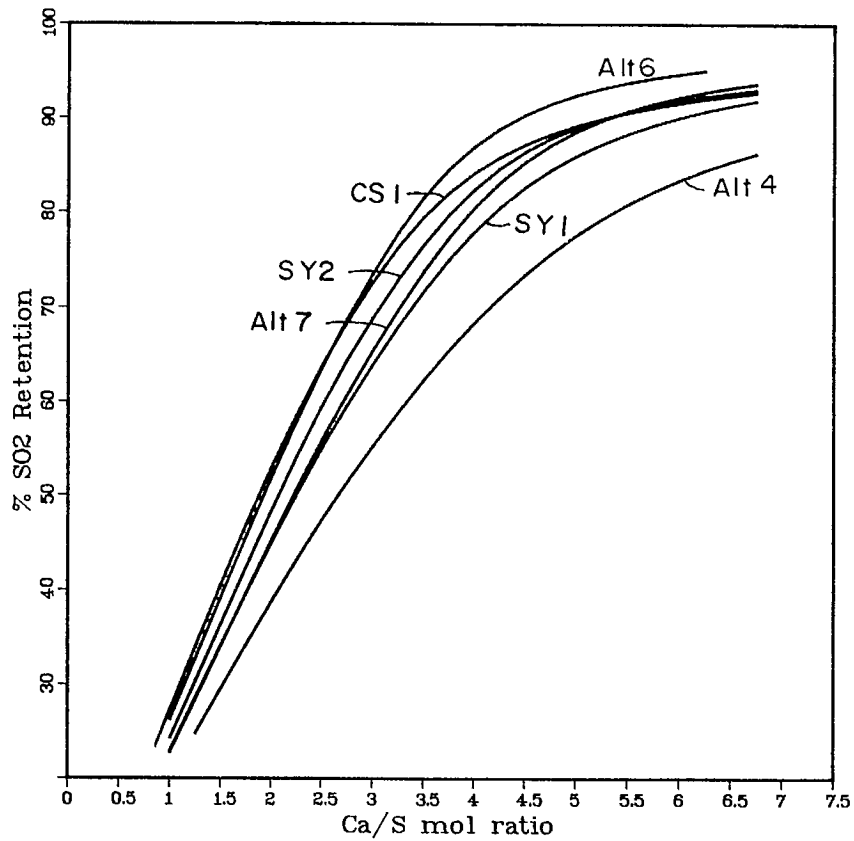
Fig. 28 - Predicted performance of Alberta sorbents in the Summerside FBC
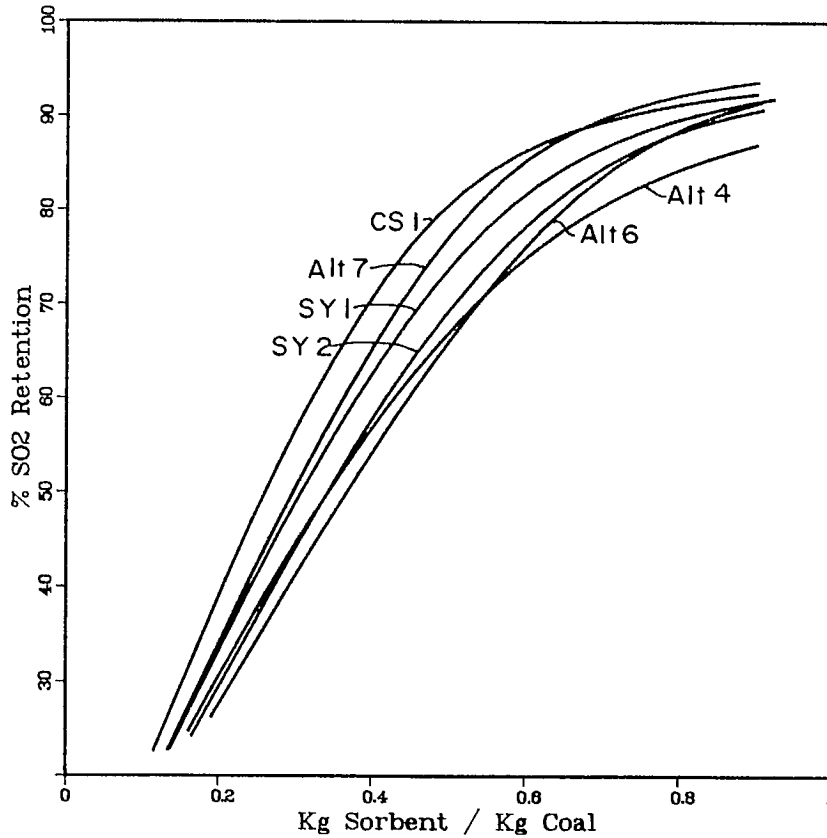
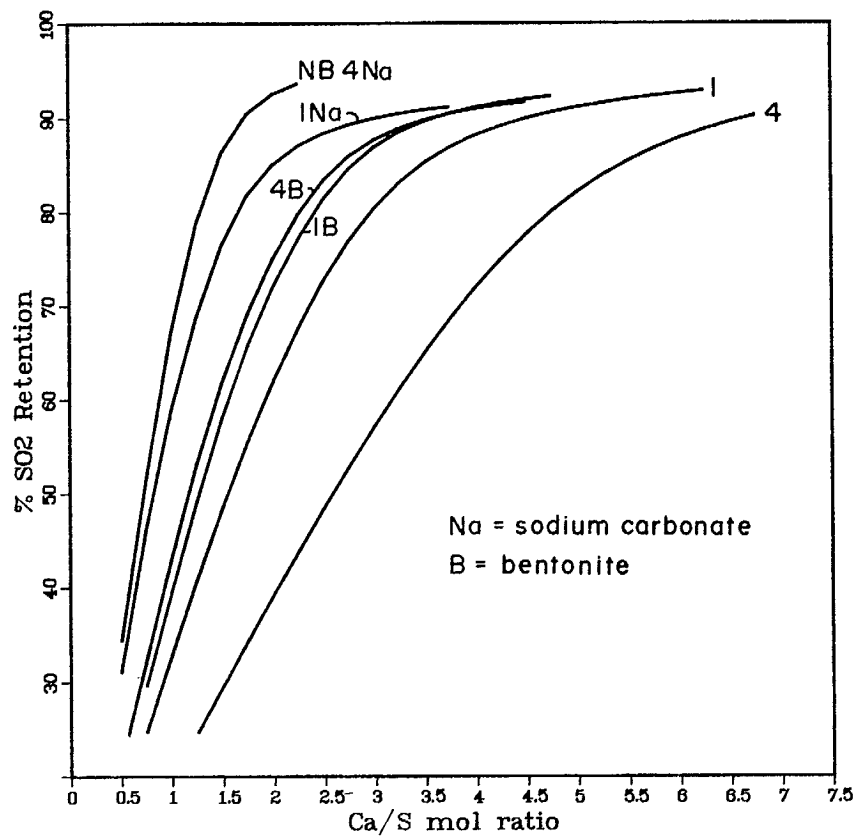Fig. 29 - Predicted performance of Alberta sorbents required for the Summerside FBC combusting 4% S coal

Fig. 30 - Predicted performance of some New Brunswick sorbents as 850-1000 µm rock and as 2000 µm pellets

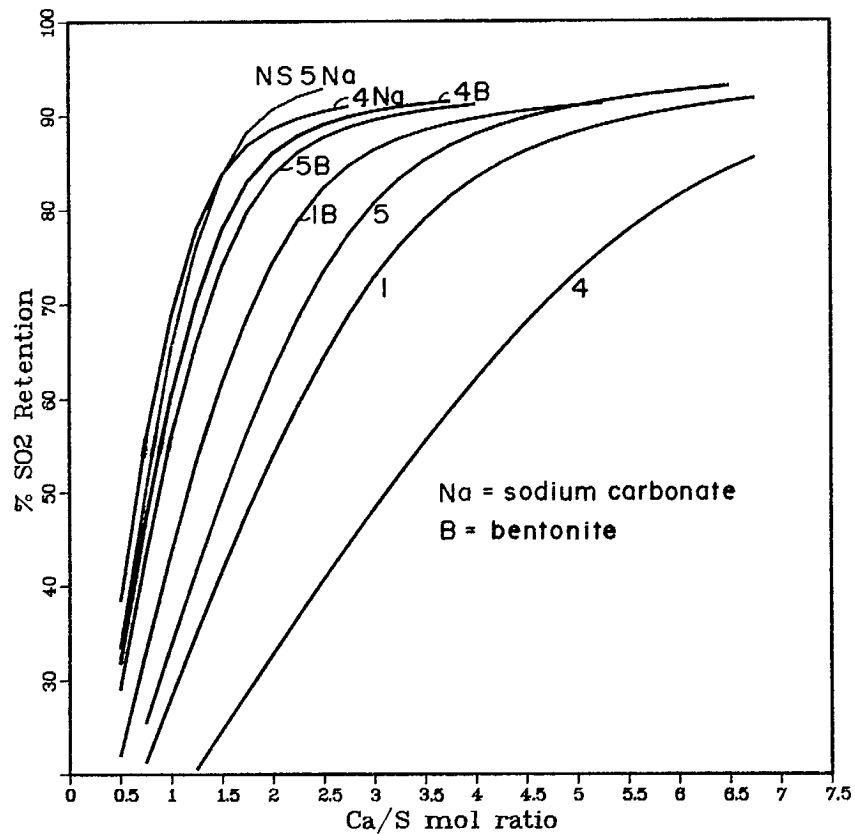

Fig. 31 - Predicted performance of some Nova Scotia sorbents as 850-1000 µm rock and as 2000 µm pellets
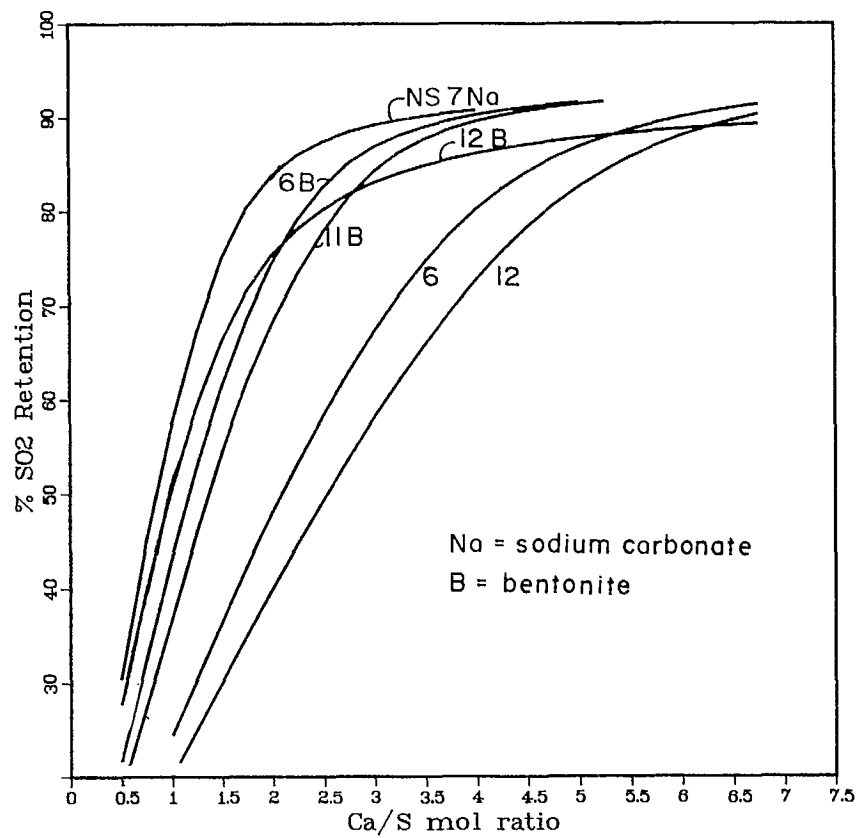
57

Fig. 32 – Predicted performance of some Nova Scotia and Alberta sorbents as
850-1000 μm rock and as 2000 μm pellets

The model does not take into account the beneficial effect of recycling cyclone fines back to the bed. Consequently, it overpredicts limestone requirements when this is done. It also assumes that all the SO_2 capture takes place in the bed whereas, in fact, some capture occurs in the freeboard. ANL has developed an addition to the basic model that does calculate freeboard sulphation (44). It indicates that the freeboard capture is only 9-10% of the total sulphur emitted from the coal. Because the freeboard capture is not a large amount and would not change the relative ranking of the sorbents, it was not included in this present work.

As can be seen in the model prediction curves, large increases in Ca/S ratio yield only small increases in SO_2 retention in the 80-90% range due to the flat nature of the curve in this region. Consequently, the model tends to overpredict limestone requirements for the higher SO_2 retention ranges. The parameters "a", "k", and "n" from the sulphation capacity equation 2 are used in the model. The higher the numerical values of "k" and "n", the more efficient is the limestone in capturing SO_2. The sulphation equations generated by the FBR method generally have higher values for "n" than obtained by the TGA method (Fig. 13). Thus, the predictions based upon FBR data should be better than from the TGA.

Economic Evaluation of Pelletization

To produce pellets of finely ground limestone would require additional, costly process operations of ball milling and pelletizing. In order to determine whether this expense is justified by the savings in sorbent, an economic evaluation was conducted by J. Palmer of MSL's Technical and Economic Evaluation Section. For this evaluation it was assumed that a 150 MW (electrical), which is equivalent to a 375 MW (thermal), AFBC unit would be built at Point Tupper, N.S. At 100% operation such a unit would burn 400 000 t/y coal rated at 30 MJ/kg containing 4% sulphur. Limestone for SO_2 capture would probably be quarried from the Glencoe deposit approximately 80 km from the power plant. This deposit has indicated quarryable reserves of 345 million tons of metallurgical and cement grade limestone (9). The reserves of the other deposits, Irish Cove and Calpo, which are within a reasonable distance from the power plant, are insufficient to supply the plant for more than a few years.

With a sulphation capacity of about 20%, the Glencoe limestone is not a particularly good sorbent. In pellet form, the capacity varies from 37 to 50% and depends upon the average particle size and the binder type. Model predictions, based on the Summerside AFBC data, and the assumption of a 90% SO_2 retention from combustion of a 4% S fuel, are given in Figure 30. This graph would indicate a required Ca/S ratio of approximately 6 for coarse limestone and from 3 to 2 for pellets. Expressed as weight, the natural rock requirement would be in the order of 1 kg/kg coal, whereas the pellet requirement would be 0.5 to 0.33 kg/kg coal. The curves for the proposed plant may vary from those shown depending upon the operating parameters and limestone particle size; however, the relative difference between the limestone and pellets should be constant.

The two cases evaluated were:

Case 1: To quarry, transport, and crush to -6300 µm an annual requirement of 400 000 t/y limestone for Ca/S ratio of 6.

Case 2: To quarry, transport, crush and pulverize to -150 µm, and then pelletize an annual requirement of 200 000 t/y limestone for Ca/S ratio of 3.

Capital Costs

Case 1: Crushing equipment, 400 000 t/y -6300 µm, operating 3 shifts, 5 days/week   = $6 208 527

Transportation, 15 trucks of 40 t capacity, operating 1 shift, 5 days/week   = $1 760 000

                                               Total capital   = $7 968 527

Case 2: Crushing, ball mill, and pelletizing equipment, 200 000 t/y operating 3 shifts, 5 days/week   = $7 242 307

Transportation, 8 trucks of 40 t capacity, operating 1 shift, 5 days/week   = $ 938 667

                                               Total capital   = $8 180 974

Operating Costs $/t limestone:	Case 1	Case 2
Transportation (including fuel, labour, maintenance operating supplies, indirect and fixed costs)	$5.54	$5.54
Comminution (raw materials, utilities, labour, maintenance, supplies, indirect and fixed costs)	$8.89	$18.85
Cost of capital investment at 12%	$2.39	$4.91
Total operating	$16.82	$29.30

A third case for a Ca/S ratio of 2 may be approximated by proportioning the costs in Case 2. Case 3 would require the quarrying, crushing, pelletizing, etc., of 132 000 t/y limestone.

Total annual limestone cost: Case 1 $6 728 000

                               Case 2 $5 860 000

                               Case 3 $3 862 600

The calculated cost of limestone sorbent for SO_2 control is a significant portion of the operating cost of an AFBC unit burning high-sulphur coal. With the quantity of limestone required as pellets being one half to one third that of natural stone, there is considerable cost advantage with the pellet method. The saving in waste disposal cost associated with the smaller quantity of material with the use of pellets was not included in the calculations. Most of the difference in operating costs of the two cases is due to the ball milling operation to produce finely ground limestone. The pelletizing operation accounts for about $2/tonne of the operating cost. Thus, if the proposed FBC unit were of the fast recirculating type, which utilizes fine limestone less than 150 μm in size, a small additional cost saving would be realized.

CONCLUSIONS

This paper summarizes the results of work done over a five-year period on the evaluation of limestone and dolomite as SO_2 sorbents in fluidized-bed combustors. A bench-scale fluidized-bed reactor was developed to test limestones in a synthetic flue gas at AFBC operating temperatures. The sulphation curves developed from this method are very similar to those obtained in the TGA method for the same samples. Over forty sorbent samples from Nova Scotia, New Brunswick, and Alberta were evaluated.

Samples tested in the 850-1000 μm particle size range, which is typical of the particles in an AFBC, were found to generally sulphate in the 20 to 30% range. A few samples have sulphation capacities above this range and a few below this range; however, for most samples about three-quarters of the limestone added to an AFBC is not utilized. Tests with fluidized beds of ash indicate that the sulphation capacity decreases with increasing iron content in the ash. The degree of the ash effect appears to be dependent upon the limestone source.

Several techniques were investigated to improve sorbent utilization. Grinding the limestone to a fine powder and pelletizing with bentonite or sodium carbonate binder were found to greatly increase the sulphation capacity of the sorbent. With the sodium carbonate binder the sulphation capacity increased by up to a factor of five times. Grinding and pelletizing to reuse sulphated bed material is another method that can more than double the utilization of the limestone. Equally effective is the hydration of used bed material wherein the formation of calcium hydroxide breaks up the sulphate layer and allows subsequent sulphation of the unreacted calcium core. An economic evaluation of the pelletizing process indicates a saving of almost 50% on sorbent costs could be achieved with this method.

The sulphation curve equation obtained from the FBR tests is combined with AFBC operating parameters in the ANL model to predict the performance of sorbents in that AFBC. The use of the model allows a more accurate method of comparing the performance of a series of sorbents. The predicted performance of Havelock limestone is in good agreement with actual data from the AFBC units at CCRL and at Summerside.

ACKNOWLEDGEMENTS

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APPENDIX A

ARGONNE MODEL FOR SO_2 CAPTURE IN FBC

Irving Johnson

Examination of the data for SO_2 capture in a FBC shows that the fraction of SO_2 generated by the oxidation of the sulfur in the coal that is retained in the bed depends on the following variables: (1) the ratio of the number of moles of calcium fed to the number of moles of sulphur fed to the combustor; (2) the superficial velocity of the fluidization air; (3) the reactivity and the type of limestone; (4) the temperature, and (5) the pressure. An understanding of these observations can be obtained by means of a simple model for the sulphur capture. This steady-state model for the sulphur capture assumes that the fluidized bed can be represented by the two-phase model, i.e., a dense phase and a bubble phase; that the SO_2 is generated in the dense phase (in which most of the coal combustion takes place); that the solids and the gases in the dense phase are completely mixed; that the bubbles are in plug flow; and that the SO_2-limestone reaction in the FBC is controlled by the same factors that control the reaction when carried out in the laboratory. It is assumed that by the proper choice of particle size and temperature in the laboratory experiments, the influence of these variables on the FBC process can be taken into account.

The sulphur balance may be written:

(dense)   (bubble)

$$S = C_1 G_1 + C_2 G_2 + F\bar{x} \qquad (1)$$

where:

S = sulphur feed rate, moles/sec
C_1 = SO_2 conc. in dense phase, moles/cm^3
C_2 = SO_2 conc. in bubble as it leaves, moles/cm^3
G_1 = Gas flow rate, dense phase, cm^3/sec
G_2 = Gas flow rate, bubble phase, cm^3/sec
F = Calcium flow rate, moles/sec
x = Ave fractional sulphation of stone leaving the bed.
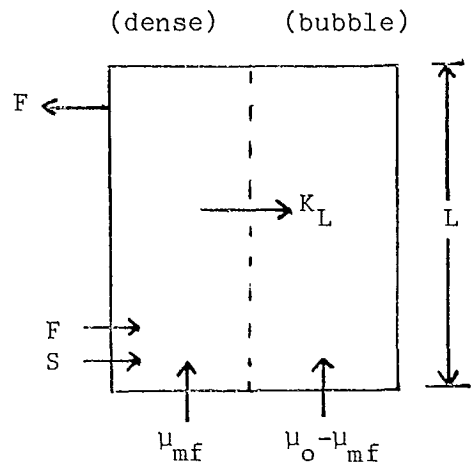
Examination of the diagram shows that:

$$G_1 = A\, u_{mf} \text{ and } G_2 = A\,(u_o - u_{mf}) \qquad (2)$$

where A is the bed cross-sectional area, u_o the superficial air velocity, and u_{mf} the minimum fluidization velocity. It is assumed that C_1, the SO_2 concentration in the dense phase, is constant. The SO_2 concentration in the bubble phase increases from zero at the bottom of the bed to some higher value

at the top of the bed. If plug flow of the bubble phase is assumed, it may be shown that the value of C_2 as the gas leaves the bed is given by:

$$C_2 = C_1 (1 - \exp [-k_L \delta L/(u_o - u_{mf})]) \tag{3}$$

where:

k_L = SO_2 exchange rate constant between dense and bubble phases
δ = volume fraction of bubbles in the bed
L = bed height.

When these expressions are substituted into the sulphur balance equation, the result may be written:

$$S = C_1 G + F\bar{x} \tag{4}$$

in which,

$$G = A u_{mf} + A(u_o - u_{mf})(1 - \exp[-k_L \delta L/(u_o - u_{mf})]) \tag{5}$$

The quantity G is, in effect, a gas flow rate (cm^3/sec). Three cases may be considered. If $k_L = 0$, i.e., no transfer of SO_2 to the bubble phase, then $G = Au_{mf}$ and the smallest value for G would be obtained. The highest retention would be obtained since no SO_2 would be lost to the bubble phase. On the other hand, if $k_L \to \infty$ then $G \to Au_o$, and the whole gas flow through the system would dilute the SO_2 and the lowest retention would be obtained. The real case is between these two extremes and is closer to the $k_L = 0$ limit.

The average fractional sulphation of the limestone that leaves the bed, x, may be calculated using the relation:

$$x = \int_o^\infty E(t) \, x(t)dt \tag{6}$$

where E(t) is the age distribution function for the material that leaves the bed, and x(t) the dependence of the fractional sulphation on time as determined from the laboratory sulphation experiments. It may be shown that for a completely mixed system:

$$E(t) = (\frac{1}{\tau})\exp(-t/\tau) \tag{7}$$

where

t = residence time for the solids in the bed
$\tau = B/F$ $\qquad\qquad$ (8)

where B = the calcium content (moles) of the bed. The conversion, x, is given by the equation:

$$x(t) = a(1-\exp(-kt^n)) \tag{9}$$

where a, k, and n are empirical constants. The constants a and n are specific for each limestone but do not have a significant dependence on the SO_2 concentration. The constant k varies with the SO_2 concentration:

$$k = k\ C^n SO_2. \tag{10}$$

When these expressions for x(t) are substituted into the sulphur balance, equation one becomes:

$$S = C_1\ G + F \int_0^\infty (1/\tau)\exp(-t/\tau)a(1-\exp(-k'(C_1 t)^n))dt \tag{11}$$

To use this equation a numerical integration method is needed. Because of the dependence of x(t) on C_1, the solution of Equation 11 must be obtained using an interactive method. When a solution has been obtained, the sulphur retention in the bed may be computed from x and the Ca/S mole ratio:

$$\text{Retention} = (Ca/S)\ \bar{x}. \tag{12}$$

Note that the Ca/S mole ratio is equal to F/S.

APPENDIX B

PROGRAM SO_2 FBI

Irving Johnson

The program begins by requesting the input of values for the empirical constants of the sulphation equation (a, k_2, and N) and the combustor conditions (S, the sulphur feed rate; B, the calcium content of the bed; and G, the effective gas flow rate).

After some DATA statements for the subscripted variables Y(I) and W(I) (explained below), the value for the SO_2 concentration used in the sulphation experiments (3000 ppm) is entered as data. The initial value of K_2 corresponds to this value of the SO_2 concentration.

The first DO loop (J=2, 20) is used to compute a series of values of the calcium feed rate, C, and the residence time, R. A key element of this program is the numerical method used to evaluate the integral for the utilization, x (sulphation):

$$x = \int_0^\infty (1/\tau)\exp(t/\tau)a(1 - \exp(-kt**n))\ dt$$

The substitution y = t/τ is made to yield the result:

$$x = \int_0^\infty \exp(-x)f(x)dx = \sum_{i-1}^m w(i)f(x(i)$$

This integral is numerically evaluated using Laguerre polynomials as described in the Handbook of Mathematical Functions (N.B.S. Applied Mathematical Series 55) pages 890 and 923. This method approximates the integral with a series:

$$x \int_0^\infty \exp(-x)f(x)dx = \sum_{i=1}^m w(i)f(x(i))$$

where the w's and x's are computed from Laguerre polynomials.

The values of Y(I) and W(I) given in the DATA statement of the program are for m = 10 (the limit on the second DO loop).

The constant k_τ^n (K*(R**N)) is evaluated and then the integral computed to obtain the average utilization x, (Z in program). The exit SO_2 concentration (in ppm) is computed from the material balance equations (Eq 4 or 11 in Appendix A). If the value of Pl is close enough to the initial value, the retention is printed out beginning at 60 in the program. If the two values (Pl and P) are not close enough, a new value of P is estimated by taking the geometric mean of the two values. It is possible for Pl to be negative, in which case one-half of the initial value is used to estimate the new guess. A new value of K is computed, corresponding to the new value for the SO_2 concentration. The utilization is again computed and the comparison repeated. A counter, L, is used to restrict the number of iterations to 100. This usually stops the program when the retentions reach values greater than 90%.

APPENDIX C

MICROSOFT BASIC PROGRAM FOR ANL MODEL FOR FBC

C.A. Hamer

```
100 CS$=CHR$(4)
110 PRINT CS$:RO$=CHR$(1):RF$=CHR$(2)
120 PRINT"      ";:PRINT RO$;
130 PRINT"* * * THIS PROGRAM CALCULATES THE PARAMETERS FOR FBCSO2MODEL * * *"
140 REM * THIS IS THE ARGONNE NATIONAL LABORATORY MODEL FOR FBC
150 REM * REFERENCE ANL REPORTS : ANL/CEN/FE-80-17 AND ANL/FE-80-10
160 REM * THIS PROGRAM BY C.A. HAMER, CANMET
170 PRINT RF$:PRINT:PRINT
180 PRINT">> These parameters are: SULPHUR FEED RATE: S; QUANTITY OF
    CALCIUM IN THE"
190 PRINT"   BED: B; and the EFFECTIVE GAS FLOW RATE: G. Do you want to
    CALCULATE"
200 PRINT"         these parameters (Y OR N)";:INPUT R$
210 IF R$="Y" THEN 220 ELSE 1550
220 PRINT CS$:PRINT">> What is today's date (DD MM YY)";:INPUT D$:PRINT
230 LPRINT CS$:PRINT"TODAY'S DATE";D$
240 PRINT>> In order to calculate S,B, and G, it is necessary to provide"
250 PRINT"   the physical parameters of the limestone and the FBC unit you"
260 PRINT"   wish to model.  Please answer the following questions:":PRINT
270 PRINT">> The following calculations assume an FBC temperature of 850°C"
280 PRINT"     If you want calculations at a different temperature you must"
290 PRINT"     give the density and viscosity of air at the desired
    temperature"
300 PRINT"     Do you want the calculations at 850C Y OR N";:INPUT R$
310 IF R$="Y" GOTO 340 ELSE 350
320 REM- THE DENSITY OF AIR AT 850C = .33 KG/CU M
330 REM- THE VISCOSITY OF AIR AT 850C = 4.5E-05 KG/M-SEC
340 DA=.33 : VA=.000045 : GOTO 380
350 PRINT"INPUT DENSITY OF AIR, KG/CU M";:INPUT DA:PRINT
360 PRINT"INPUT VISCOSITY OF AIR AT DESIRED TEMPERATURE, KG/M-SEC"
370 INPUT VA
380 PRINT
390 PRINT">> Which FBC unit is being modelled ";:INPUT B$:PRINT
400 LPRINT" THE FBC UNIT BEING MODELLED IS "; B$
410 PRINT">> What is the limestone identification ";:INPUT A$:PRINT
420 LPRINT" THE LIMESTONE IDENTIFICATION IS "; A$
430 PRINT">> What is the coal feed rate in KG/H";:INPUT C:PRINT
440 LPRINT" THE COAL FEED RATE,KG/H=";C
450 PRINT">> What is the % SULPHUR in the coal";:INPUT D:PRINT
460 LPRINT" THE % SULPHUR IN THE COAL="; D
470 PRINT">> What is the % CaCO3 of the limestone";:INPUT CA:PRINT
480 LPRINT" The % CaCO3 OF THE LIMESTONE="; CA
490 PRINT">> What is the % MgCO3 of the limestone";:INPUT MG:PRINT
500 LPRINT" The % MGCO3 OF THE LIMESTONE="; MG
510 PRINT">> What is the bulk density of the LIMESTONE FEED, G/CC?"
```

```
520 PRINT" This density is normally about 1.5 g/cc";:INPUT F:PRINT
530 REM * THE BULK DENSITY IS DETERMINED BY GENTLY POURING A SAMPLE OF
540 REM    * LIMESTONE FEED INTO A TARED GRADUATED CYLINDER
550 LPRINT " THE BULK DENSITY OF THE LIMESTONE FEED, G/CC=";F
560 PRINT">> What is the raw limestone particle density, G/CC"
570 PRINT"          This density is normally about 2.5 g/cc";:INPUT P:PRINT
580 LPRINT "THE RAW LIMESTONE PARTICLE DENSITY, G/CC=";P
590 PRINT">> What is the sulphation capacity (Decimal Fraction)";:INPUT
    X:PRINT
600 LPRINT"THE SULPHATION CAPACITY, DECIMAL FRACTION=";X
610 PRINT">> Is the above input correct";:INPUT R$
620 IF R$="Y" THEN 630 ELSE 390
630 PRINT">> It is necessary to know or to calculate the average particle
    size"
640 PRINT"  of the limestone. Do you know this value (TYPE 1) or do you
    wish"
650 PRINT"  to calculate it from a sieve analysis (TYPE 2)";:INPUT R$
660 IF R$="1" GOTO 678 ELSE 700
670 PRINT">> What is the average particle size of the LIMESTONE FEED
    (METERS)";:INPUT DP
680 LPRINT"THE AVE PARTICLE SIZE OF LIMESTONE FEED, METERS=";DP
690 GOTO 990
700 DIM SS(10),WT(10),SA(10),SW(10)
710 PRINT">> How many SIEVES were used, including the PAN";:INPUT N
720 FOR I=1 to N-1
730 PRINT">> What is the SIZE in MM, SIEVE";1;:INPUT SS(I)
740 NEXT I
750 PRINT"Is the above correct";:INPUT R$
760 IF R$="Y" THEN 770 ELSE 710
770 FOR I=1 TO N-1
780 PRINT">> What is the WEIGHT FRACTION MATERIAL RETAINED on SIEVE";I;
790 INPUT WT(I)
800 NEXT I
810 IF I=N THEN 820
820 PRINT">> What is the WEIGHT FRACTION MATERIAL RETAINED in the PAN"
830 INPUT WT(I)
840 PRINT"Is the above correct";:INPUT R$
850 IF R$="Y" THEN 860 ELSE 770
860 SW(1)=WT(1)/SS(1)
870 FOR I=2 TO N-1
880 SA(I)=SS(I-1)+SS(I)
890 SW(I)=2*WT(I)/SA(I)
900 NEXT I
910 SW(N)=WT(N)/SS(N-1)
920 ZS=0
930 FOR I-1 TO N
940 ZS=ZS+SW(I)
950 NEXT I
960 DP=1/1000*ZS)
970 PRINT">> The CALCULATED MASS AVERAGE PARTICLE SIZE (meters)=";DP;:PRINT
980 LPRINT">>The CALCULATED MASS AVERAGE PARTICLE SIZE (meters)=";DP
990 PRINT
```

```
1000 PRINT">> What is the STATIC BED HEIGHT (meters)";:INPUT H:PRINT
1010 LPRINT"The STATIC BED HEIGHT, METERS="; H
1020 PRINT">> What is the EXPANDED BED HEIGHT (Meters)";:INPUT L:PRINT
1030 LPRINT"THE EXPANDED BED HEIGHT, METERS="; L
1040 PRINT">> What is the FLUIDIZING VELOCITY, M/SEC";:INPUT U:PRINT
1050 LPRINT "THE FLUIDIZING VELOCITY, M/SEC"; U
1060 PRINT">> How many NOZZLES are in the distributor plate";:INPUT NO:PRINT
1070 LPRINT"NUMBER OF NOZZLES IN THE DISTRIBUTOR PLATE="; ND
1080 PRINT">> What is the AREA OF THE BED in SQ METERS";:INPUT A:PRINT
1090 LPRINT" THE AREA OF THE BED IN SQ METERS="; A
1100 PRINT">> Is the above input correct";:INPUT R$
1110 IF R$="Y" THEN 1120 ELSE 1000
1120 S= 1000*C*D/(100*32*60)
1130 PRINT "SULPHUR FEED RATE, S, MOLE/MIN=";S:PRINT
1140 LPRINT "SULPHUR FEED RATE, S, MOLE/MIN=";S
1150 REM * THE QUANTITY OF CALCIUM IN THE BED = VOLUME OF STATIC BED *
1160 REM      BULK DENSITY * A FACTOR OF 1.1 * CaCO3 / MOLECULAR WT
1170 B=A*H*F*CA*118
1180 PRINT "QUANTITY OF CALCIUM IN BED, B, MOLE=";B:PRINT
1190 LPRINT"QUANTITY OF CALCIUM IN BED, B, MOLE=";B
1200 PRINT
1210 REM * CALCULATION OF PARTIALLY SULPHATED LIMESTONE DENSITY
1220 REM          BASED ON RAW DENSITY AND ANALYSIS
1230 Z=P*CA/100
1240 RR=P*MG*40/(100*84)
1250 Y=Z*.56+(P-Z-RR)
1260 T=Z*1.36+(P-Z-RR)
1270 PB=X*T+(1-X)*Y
1280 PRINT *CALCULATED DENSITY OF BED MATERIAL=";PB:PRINT
1290 LPRINT"CALCULATED DENSITY OF BED MATERIAL=";PB
1300 NGA=(DP^3)*DA*9.8*(PB*1000-DA)/VA^2
1310 PRINT*THE VALUE OF GALILEO'S NUMBER =";NGA:PRINT
1320 IF NGA<10^5 THEN 1330 else 1340
1330 UMF=.00134*VA*(NGA .89)/(DP*DA):GOTO 1350
1340 UMF=.8426*VA*(NGA .682)/(DP*DA)
1350 PRINT "MIN FLUIDIZING VEL, UMF, M/SEC=";UMF:PRINT
1360 LPRINT "MIN FLUIDIZING VEL, UMF, M/SEC=";UMF
1370 V=(L-H)/L
1380 PRINT"VOLUME FRACTION OF BUBBLES IN THE BED =";V:PRINT
1390 REM * FOLLOWING CALCULATES AVE BUBBLE DIA
1400 DBO=,939*(A*(U-UMF)/ND)^.4
1410 DR=SQR(4*A/3.142)
1420 M=.15*L/DR
1430 DBM=1.64*(A*(U-UMF))^.4
1440 IF DR <DMM THEN 1450 else 1460
1450 J=DR-(DR-DBO)*EXP(-M):GOTO 1470
1460 J=DBM-(DBM-DBO)*EXP(-M)
1470 KL=.11/J
1480 PRINT"THE GAS EXCHANGE COEFF, KL=";KL:PRINT
1490 Q=KL*L*V/(U-UMF)
1500 G=A*(UMF+(U-UMF)*(1-EXP(-Q)))*60000!
1510 PRINT "THE EFFECTIVE GAS FLOW RATE, G, L/MIN=";G
1520 LPRINT "THE EFFECTIVE GAS FLOW RATE, G, L/MIN=";G:GOTO 1740
1530 CS$=CHR$(4)
```

```
1540 PRINT CS$:RO$=CHR$(1):RF$=CHR$(2)
1550 PRINT RO$
1560 PRINT"* * * THIS PROGRAM CALCULATES LIMESTONE SULPHATION CA/S RATIO * * *"
1570 REM * THE FOLLOWING IS A MODIFIED VERSION OF IRVING JOHNSON'S
1580 REM * SO2FB1" PROGRAM, REVISION 31 DEC 80
1590 PRINT RF$:PRINT:PRINT:PRINT
1600 PRINT"WHAT IS THE FBC UNIT BEING MODELLED";:INPUT B$:PRINT
1610 LPRINT "THE FBC UNIT BEING MODELLED IS "; B$
1620 PRINT">> LIMESTONE IDENTIFICATION";:INPUT A$:PRINT
1630 LPRINT "LIMESTONE IDENTIFICATION IS "; A$
1640 PRINT">> INPUT SO2 FEED RATE, MOLES/MIN";:INPUT S:PRINT
1650 LPRINT" INPUT SO2 FEED RATE, MOLES/MIN"IS ";S
1660 PRINT">> WHAT IS % SULPHUR IN THE COAL";:INPUT D:PRINT
1670 LPRINT" THE % SULPHUR IN THE COAL="; D
1680 PRINT">> INPUT % CaCO3";:INPUT CA:PRINT
1690 LPRINT" INPUT % CaCO3 OF LIMESTONE ";CA
1700 PRINT">> INPUT QTY OF CALCIUM IN THE BED, MOLES";:INPUT B:PRINT
1710 LPRINT" QTY OF CALCIUM IN THE BED, MOLES"; B
1720 PRINT">> INPUT EFFECTIVE GAS FLOW, L/MIN";:INPUT G:PRINT
1730 LPRINT" EFFECTIVE GAS FLOW, L/MIN"; G
1740 PRINT">> INPUT A,K,N OF SULPHATION EQN";:INPUT AA,K2,N:PRINT
1750 LPRINT" INPUT A,K,N OF SULPHATION EQN ARE"; AA,K2,N
1760 PRINT">> IS THIS DATA FROM THE FB REACTOR OR TGA";:INPUT C$:PRINT
1770 LPRINT" THIS DATA ARE FROM "   ;C$
1780 PRINT">> INPUT SO2 CONC OF TEST";:INPUT P2:PRINT
1790 LPRINT" INPUT SO2 CONC OF TEST IS "; P2
1800 PRINT">> Is the above input correct";:INPUT R$
1810 IF R$="Y" THEN 1820 ELSE 1600
1820 FOR I=1 TO 10
1830 READ Y(I),W(I)
1840 NEXT I
1850 K=K2:P=P2
1860 PRINT:PRINT:PRINT RO$:PRINT A$:PRINT RF$:PRINT
1870 GOSUB 2230:          REM PRINT TITLE
1880 FOR J=2 TO 20
1890 L=0
1900 C=.5*J*S
1910 R=B/C
1920 K1=K*(R^N)
1930 L=L+1
1940 IF L >100 THEN END
1950 Z=0
1960 REM LOOP INSERT
1970 FOR I=1  to 10
1980 E=K1*(Y(I)^N)
1990 IF E>30 then 2020
2000 F=AA
2010 GOTO 2030
2020 F=AA*(1-EXP(-E))
2030 Z=Z+F*W(I)
2040 NEXT I
2050 P1=2.24E+07/G*(S-C*Z/100)
2060 IF ABS(P1-P)<.1 THEN 2140
```

```
2070 IF P1>0 then 2090
2080 P1=.5*P
2090 P1=(P1+P)/2
2100 P1=SQR(P1*P)
2110 K=K*((P1/P)^N)
2120 P=P1
2130 GOTO 1920
2140 CAS=.5*J
2150 RET=CAS*Z
2160 SC=100*D*.5*J/(CA*32)
2170 PRINT
2180 PRINT USING" ##.# ";CAS;:PRINT"    ";
2190 PRINT USING" ##.#### ";Z;RET;SC
2200 LPRINT USING" ##.# ";CAS;:PRINT"    ";
2210 LPRINT USING"  ##.#### ";Z;RET;SC
2220 NEXT J
2230 PRINT "(CA/S)";TAB(12);"UTIL";TAB(22);"RET'N";TAB(35);"KG STONE/KG COAL"
2240 LPRINT"(CA/S)";TAB(12);"UTIL";TAB(22);"RET'N";TAB(35);"KG STONE/KG COAL"
2250 PRINT:PRINT
2260 RETURN
2270 DATA .13779,.308441,.72945,.40113
2280 DATA 1.80834,.218068,3.40143,.0620875
2290 DATA 5.5525,8.50152E-03,8.33015,7.53008E-04
2300 DATA 11.8438,2.82592E-05,16.2792,4.24931E-07
2310 DATA 21.9966,1.83956E-09,29.9207,9.91183E-13
2320 END.
```