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CALCIUM SULPHIDE FORMATION IN SOLID WASTES FROM CIRCULATING  
FLUIDIZED BED COMBUSTORS

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CALCIUM SULPHIDE FORMATION IN SOLID WASTES FROM  
CIRCULATING FLUIDIZED BED COMBUSTORS

by

E.J. Anthony<sup>1</sup>, J.R. Stephenson<sup>2</sup> and A.P. de Iribarne<sup>3</sup>

ABSTRACT

High concentrations of CaS  $\leq 6\%$  in solid residues from a sub-scale circulating fluidized bed combustor (CFBC) operated by the New Brunswick Research and Productivity Council (RPC) have suggested that fluidized bed residues may be more hazardous than previously thought. To provide a better information base, residues were analyzed for CaS from a variety of bubbling and circulating bed combustors. Results from bubbling beds burning high sulphur fuels in the presence of limestone showed only minor concentrations of CaS (0.2%). Results from several other CFBC's indicated lower concentrations of CaS ( $<1\%$ ) than seen initially in the RPC rig and that lower concentrations were produced in larger rigs. It is concluded that CaS can be generated either in the lower section of a circulating bed or in the hot cyclone and return leg under reducing conditions, but that the high levels found in the RPC unit are probably atypical. Experimental evidence seems to suggest that residues from commercial CFBC's are likely to contain CaS levels comparable to those found in bubbling bed units.

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## INTRODUCTION

In March 1985 Dearborn Environmental Consulting Services was awarded a contract by the Canadian Electrical Association (CEA) to carry out characterization studies of solid wastes from circulating fluidized bed (CFB) combustion. The project's prime objective was to combust a wide range of Canadian solid fuels with limestone in a pilot-scale atmospheric CFB unit in order to generate representative samples of solid waste and then to characterize them and produce a database on their properties. Secondary objectives were to identify potential areas of concern regarding the management of such wastes and to recommend areas requiring further research.

The Dearborn proposal called for the wastes to be generated in the pilot-scale CFB facility owned by GA Technology Inc., San Diego, California. By January 1986 it was apparent that GA Technology would not be able to complete the pilot-scale work within the time frame set by the CEA project. Consequently, Dearborn subcontracted the pilot-scale work to the RPC which had recently commissioned a new 130 mm (5 in.) diameter CFB combustor.

The actual test work was carried out by RPC in March 1986 and published as a report to the CEA (1). It involved 11 successful trials with combinations of four coals and three limestones. The test matrix is given in Table 1 and the operating conditions are given in Table 2.

Analysis of the test results showed that the calcium utilization was at least equivalent to good bubbling bed performance although "steady state" had not been achieved. However, significant quantities of CaS (1-6%) were found in the RPC solid residues and if corrected for silica sand, CaS concentrations as high as 19% were predicted. This would adversely affect the cost of disposal of CFB waste solids and probably make it impossible to utilize these solids if these results were found to be typical for normal CFB combustion processes. Therefore this work is aimed at determining how CaS is formed in CFB systems and predicting the typical levels of this contaminant.

## EXPERIMENTAL RESULTS FROM RPC

Table 3 gives the chemical composition of the various samples taken from the RPC rig during the test series. The designation B in Table 3 refers to bed material sampled from a standpipe in the J valve section of the

combustor (Fig. 1). BH refers to material taken from the baghouse. The total sulphur  $\text{CaSO}_4$ ,  $\text{CaCO}_3$  and C were determined by wet chemistry, the total Ca by means of both X-ray fluorescence and neutron activation and the free CaO by acidimetric back titration. The CaS was then calculated by difference from the analysis of total sulphur and sulphate sulphur, the presence of CaS having been confirmed by X-ray diffraction (1).

The most striking feature of the results in Table 3 is the very high concentrations of CaS in the ash residues (up to 6%). Also it is apparent that, except for runs 7 and 10, most of the CaS is found in the "bed material" whereas CaS concentrations in the baghouse ash are typically 1% or less. Figure 2 shows that the CaS concentrations seem to correlate with the C content of the "bed material", determined after the CEA study on archival samples from the RPC unit (2), but the CaS concentrations in the baghouse do not show any dependence on the C content of either solid stream associated with the standpipe or the baghouse.

These facts seem to support the idea that the CaS is being formed in the cyclone/standpipe section of the RPC combustor an alternative possibility however is that CaS is being formed in the bed and concentrated in the cyclone and standpipe (3).

#### FORMATION OF CaS IN FBC SYSTEMS

The presence of CaS in wastes from solids in AFBC systems has been previously identified (4-6). However the concentrations determined were so low that Sun et al. (5) state that CaS is not a problem for once-through FBC systems as opposed to systems with a sorbent regeneration feature, while Constable et al. (6), who worked with Canadian samples, conclude that elemental sulphur and sulphides are negligible.

Unfortunately, the actual amounts of CaS are not quantified. However sulphides have been occasionally detected by smell as  $\text{H}_2\text{S}$ , when solids from FBC residue samples are acid digested as part of the process of analysis (7). Since  $\text{H}_2\text{S}$  can be sensed by the human nose at the ppm level (8) this has not been judged as significant and no actual measurements for CaS have been made. Regarding CaS in CFB wastes, up to the time of writing there have been few or no sources of such wastes in Canada and no measurements were made prior to the CEA study (1).

The subject of CaS formation in CFB systems is therefore essentially new and in order to understand how this compound is produced it is necessary to consider the chemistry involved. CaS can be formed in either packed or fluidized bed gasifiers (9) by means of the reaction:



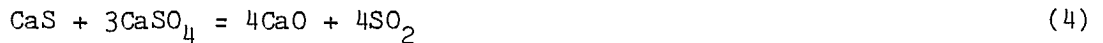
Another possible reaction that may occur under reducing conditions (10) is:



CaS can also be formed directly from  $\text{CaSO}_4$  by means of CO either in the gas phase or generated from the char or carbon when in an intimate mixture with the  $\text{CaSO}_4$  via the reaction:



The  $\text{CaSO}_4$  so formed may then also react further with any remaining  $\text{CaSO}_4$  to give CaO and  $\text{SO}_2$  by means of the reaction:



Whether CaS or CaO is formed during the reduction of  $\text{CaSO}_4$  is strongly dependent on the C/S molar ratio with low relative concentrations ( $\sim 1:2$ ) favouring the formation of CaO and high relative concentrations ( $\sim 2:1$ ) preferentially producing CaS (11,12). Once formed, CaS may also be destroyed by  $\text{O}_2$  and steam (13,14). The various possible reactions and temperatures for these to occur are shown diagrammatically in Fig. 3.

From these reactions it is clear that CaS may be formed either in the bed under reducing conditions via reaction 1 to 3 or in the case of a CFB also in the hot cyclone/return leg of the unit via reaction 3. In many cases the combustion air is staged in CFB units so that the lower portion operates under reducing conditions. This means there are two possible regions in a CFB which might be capable of producing CaS (7).

Since the reduction of  $\text{CaSO}_4$  occurs at temperatures above  $680^\circ\text{C}$  and reactions 1 to 3 require reducing conditions it is clear that CaS will not be produced in the bed, cyclone, or heat exchanger (used to protect the baghouse) of a bubbling bed. It should also not be produced in the heat exchanger and baghouse of a circulating bed (7).

It should be noted that the current design of the RPC combustor has a large standpipe (300 mm diameter) pipe which is typically filled with 250 kg of sand. Since the solid recycle rate is about 35 kg/min, entrained solids travelling at or near the gas velocities in the combustor might be expected to spend a second or so in the combustor but up to 7 min in the return leg of the combustor. This suggests that if reaction 3 occurs in CFB's it might be particularly important in the RPC combustor in its present configuration.

#### EXPERIMENTAL RESULTS

The first question that arose from the data in the CEA report was whether the analysis using the "difference method" for CaS developed and carried out by de Iribarne for Dearborn could in some way be in error. In order to investigate this we developed alternative methods of measuring CaS directly and cross checked the results from a number of selected samples from the CEA study. The first method used involved digestion of the samples in acetic acid and direct determination of the  $\text{H}_2\text{S}$  produced by means of the Fisher sulphur analyzer. This was quickly abandoned in favour of an Arsenazo III titration method because it required the use of a high purity CaS standard which was found to be unavailable at the time. However, all three methods are in good agreement as shown in Table 4.

Although the other methods give values which in the worse case are 25% lower than those determined for the CEA study, the agreement is still sufficiently good to validate the Dearborn/CEA work. Attempts to determine whether the discrepancy was due to the presence of another sulphur form were unsuccessful as the highest concentrations of  $\text{CaSO}_3$  detected were 0.15% or less and no elemental sulphur has been found (15). However, the differences are of academic interest only and there can be no doubt that the results reported by Dearborn to the CEA are essentially correct.

The second question that arose was what concentrations of CaS, if any, were actually present in solid residues produced by bubbling beds.

Although this question cannot be answered in a completely unambiguous manner it was decided to determine the CaS concentrations in a number of archival samples from various Canadian bubbling bed facilities.

The results are shown in Table 5 and clearly indicate that negligible amounts of CaS are produced in the bed solids from bubbling bed unit (<0.2%). However larger quantities can be found in the elutriated solid streams, i.e., cyclone and baghouse material. The greatest amounts are found in the baghouse material, in the worst case so far examined up to 0.9% CaS from a pilot scale bubbling bed rig. The CaS concentrations in the cyclone solids so far examined seemed to correlate with the cyclone carbon content but no such correlation can be seen with any of the other solid streams (16). Only a few such samples have been examined so far and it is not clear whether this is a general results or simply an artifact of the current data set investigated. In any case given the likely reactions that produce CaS it seems probable for bubbling bed samples that CaS is being produced in the bed by mean of reaction 1 to 3 and elutriated before it can be completely destroyed by the reactions that occur in O<sub>2</sub> rich regions of the bed and freeboard and is not being formed in the cyclone or the baghouse.

CaS concentrations from larger FBC units seem, if anything, typically less than those seen from the Queen's pilot scale unit and this is what one would expect if the CaS originates in the bed of bubbling bed FBC units since the elutriated solids have a longer time to react under oxidizing conditions. The overall results clearly confirm the observations of earlier worker that CaS concentrations are negligible in solid residues from bubbling beds. Typically they appear to be 0.2% or less although pilot scale residues do occasionally show higher levels in the elutriated solid streams.

The final question is what are the likely concentrations that are produced in other CFB units and are they similar to those seen in the RPC combustor. In order to investigate this problem solid samples were taken from three CFB units burning Canadian fuels and limestones:

1. The bench scale CFB at the Mineral Sciences Laboratories (MSL). This unit has an internal diameter of 100 mm and is 2.8 m high.
2. The pilot scale rig at the University of British Columbia (UBC). This Unit is run under contract to CANMET and is 150 mm square and is 7 m high.

3. The Hans Ahlstrom (HA) reactor in Finland. This unit, which was employed in a recent contract to burn Syncrude coke and Athabasca limestone, has an internal diameter of 600 mm and is 8.5 m high.

In addition to the samples generated by RPC, Dearborn was also supplied with one sample generated by a Lurgi pilot plant in Germany (results designated as S-B-11 and S-BH-11 in the CEA report). We have little data on the plant beyond the fact that it burnt Minto coal and used a mixture of Albert County oil shale and Sauerlaender limestone with a combined Ca/S molar ratio of 2.4. However the plant must be considerably larger than the RPC facility because it employed about seven times the coal feed rate used with the RPC runs (17). The results from some of these trials are presented in Table 6.

These results clearly show that CaS also occurs in other rigs. However there are a number of important differences between them and the results produced from the RPC combustor. First, none of the concentrations are as large as the worst cases seen with the CEA study. This difference is even more marked when one realizes that the samples obtained from the various rigs were obtained under steady state conditions. If the results from the CEA study are corrected to a sand free basis then concentrations as high as 19% are predicted. This suggests that the results obtained from the RPC unit for CaS are not typical of CFB combustors in general.

The second conclusion that can be drawn is that the highest concentrations of CaS are likely to be found in reducing regions such as the return leg of the CFB combustors. Since this is where the samples designated as bed samples in the CEA study were drawn it is not altogether surprising that these showed elevated CaS concentration. Third, and perhaps most important these results suggest that larger units produce residues with lower CaS concentrations.

RPC has recently conducted some trials with Devco Prince and Elmtree limestone in which all of the combustion air was introduced in the bottom of the combustor. The results were 0.02% of CaS in the bed material, 0.09% from the secondary cyclone and 0.04% in the baghouse solids. Since 40% of the RPC combustor could be under reducing conditions in normal operation this may explain the high CaS concentrations seen in the samples generated for the CEA study. This in turn would suggest that the method by which CaS is produced



in the CFB units is by reactions 1 to 3 and collected in the return leg. However some caution is necessary in accepting this interpretation as low concentration of CaS were occasionally seen in the samples previously produced for the CEA, e.g., S-BH-4 and the standpipe carbon associated with this run is also the lowest seen from the samples generated by RPC, i.e., 0.12%. This may mean that by changing the conditions, the environment in the return leg has also been changed and that notwithstanding CaS is formed in the return leg. Clearly more work is necessary in order to elucidate the mechanism of formation of CaS in CFB systems.

### CONCLUSIONS

CaS can be produced in CFB systems, however the recent high levels (up to 6%) seen in a major study for the CEA do not appear to be typical of the technology. Instead, levels of 0.2% or less which are similar to those found in larger bubbling bed units, are more usual. Larger units seem to be associated with lower levels of CaS.

The mechanism by which CaS is formed in CFB units is not clear and may involve formation in the bed and concentration in the hot cyclone/return leg or direct formation in the return leg as well. Regardless of which mechanism predominates, the highest concentrations of CaS in the results for the RPC combustor seem to be found in the return leg. This suggests that waste solid withdrawal should be restricted to the bed, heat exchanger and baghouse if possible and that only oversized solids should be withdrawn from the return leg or any other area which is under reducing conditions.

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Table 1 - Test matrix for RPC combustion trials

Run	Coal	Limestone	Ca/S molar ratio
1	Devco Prince	Havelock	1.5
2	Devco Prince	Exshaw	2.0
3	Devco Prince	Elmtree	2.5
4	Poplar River	Havelock	2.0
5	Poplar River	Elmtree	1.5
6	Poplar River	Elmtree	1.5
7	US Bituminous	Havelock	2.5
8	US Bituminous	Exshaw	1.5
9	US Bituminous	Elmtree	2.0
10	Minto	Havelock	2.4
12*	Devco Prince	Elmtree	2.5

\*A long duration test. Test 11 in the Dearborn report (1) to the CEA was for a comparison sample generated in a Lurgi pilot facility using New Brunswick Minto coal, oil shale and a German limestone.

Table 2 - Operating conditions for CFB test work at RPC

Bed temperature	850 + 25°C
Air distribution: Primary	60%
Secondary	40%
Superficial gas velocity	5-8 m/s
Coal feed rate*	10-15 kg/h
Start up material	Silica sand
Mean size consist of sand	1 mm
Coal size consist	3.8 mm x 0
Limestone size consist	2.0 mm x 0
Test duration** (after stable air, fuel feed rates and gas composition were achieved)	Minimum 12 h

\*Chosen to achieve desired excess air at the set operating condition.

\*\*The test durations were recognized to be insufficient to give two or three "bed turnovers" and were chosen on the basis of economic constraints.

Table 3 - Composition of the active chemical species in the solid samples from the RPC combustor

Sample	CaS	CaSO <sub>4</sub>	CaCO <sub>3</sub>	Free CaO	CaSO <sub>4</sub> carbon
S-B-1	5.3	4.2	2.0	9.3	6.4*
S-BH-1	0.4	8.8	1.8	14.6	30.8
S-B-2	1.8	0.8	7.1	1.0	0.8
S-BH-2	1.1	6.4	1.4	1.9	22.2
S-B-3	4.8	5.9	5.7	10.2	3.6*,2.7
S-BH-3	1.3	16.7	1.6	15.2	15.0
S-B-4	3.0	2.4	2.5	15.1	0.8*,0.8
S-BH-4	0.0	14.9	2.3	20.0	2.72
S-B-5	1.4	0.7	2.5	5.7	0.6
S-BH-5	0.0	12.1	5.0	11.0	5.4
S-B-6	0.9	1.3	0.2	8.1	-
S-BH-6	0.3	7.4	6.4	9.8	2.6
S-B-7	1.0	2.5	2.3	6.4	-
S-BH-7	1.3	8.2	4.8	9.4	22.1
S-B-8	1.4	2.6	8.9	0.7	1.0
S-BH-8	1.0	4.2	1.8	1.9	24.7
S-B-9	2.7	4.8	2.5	10.6	1.8
S-BH-9	1.0	8.9	2.3	5.6	19.2
S-B-10	2.5	0.7	2.3	5.5	0.8
S-BH-10	6.3	8.4	4.3	36.0	10.2
S-BH-12	3.8	6.7	2.7	14.6	-
S-BH-12	2.6	15.0	2.3	21.0	10.9

The carbon content of bed samples was not determined in the original work and was subsequently measured from archival samples, where available using a CHN analyzer at Queen's University (samples designated\*) or at CANMET using a loss on ignition method developed at the Combustion and Carbonization Research Laboratories (2).

Table 4 - Comparison of the CaS analysis for Dearborn

Reporter/ method	% CaS			
Sample	S-B-1	S-B-3	S-B-4	S-BH-10
Dearborn	5.31	4.79	2.99	6.30
Queen's	4.54	-	2.20	-
Fisher*				
Queen's	4.48	3.6	2.05	5.60
Arsenazo III				

\*Corrected assuming the standard's purity of 69.8%

Table 5 - Analysis of bubbling bed solid residues for CaS

Samples origin	Fuel/limestone	Run No.	Type	% CaS
Queen's pilot plant (0.154 m <sup>2</sup> )**	Devco Prince/ Calpo	850515	Bed	0.00
Queen's pilot plant	Minto/ Havelock	850606	Bed	0.04
Queen's pilot plant	Minto/ Havelock	850606	Cyclone	0.09
Queen's pilot plant	Minto/ Havelock	850606	Baghouse	0.92
Queen's pilot plant	Syncrude/ Athabasca	840827	Bed	0.00
Queen's pilot plant	Syncrude/ Athabasca	840827	Cyclone	0.29
Queen's pilot plant	Syncrude/ Athabasca	840827	Baghouse	0.29
Summerside plant*	Devco Prince/ Havelock	Nov. 24, 1983	Bed	0.13
Point Tupper plant (1 m <sup>2</sup> )**	Lingan/ Irish Cove	Run 10	Bed	0.02
Point Tupper plant	Lingan/ Irish Cove	Run 10	Cyclone	0.02
Point Tupper plant	Lingan/ Irish Cove	Run 10	Baghouse	0.00

\*In the Summerside Demonstration Plant the solid streams discharged from the bed and baghouse are collected together

\*\*Bed area



Table 6 - Analysis of CFB residues for CaS

System	Fuel/Sorb.	Run No.	Bed	Recycle	Heat Ex.	Baghouse
MSL	Syncrude/ Athabasca	A1099-86	-	-	1.33	0.70
MSL	Minto/ Elmtree	860919	1.84	-	1.14	1.04
MSL	Minto/ Elmtree	860925	0.43	0.59	0.27	0.36
MSL	Minto/ Havelock	860930	0.25	0.78	0.25	0.25
MSL	Minto/ Elmtree	861002	0.13	0.35	0.14	0.18
Lurgi	Minto/ Limestone, Oil shale	S-11	0.00	-	-	0.00
UBC	Esso/ Green Valley	113	0.04	0.02	0.11	0.38
UBC	Esso/ Green Valley	114	0.02	0.02	-	-
UBC	Esso/ Green Valley	115	0.04	0.04	-	0.09
HA	Syncrude/ Athabasca	16	0.14	1.19*	-	0.00

\*The fuel is introduced via the return leg for the HA CFBC

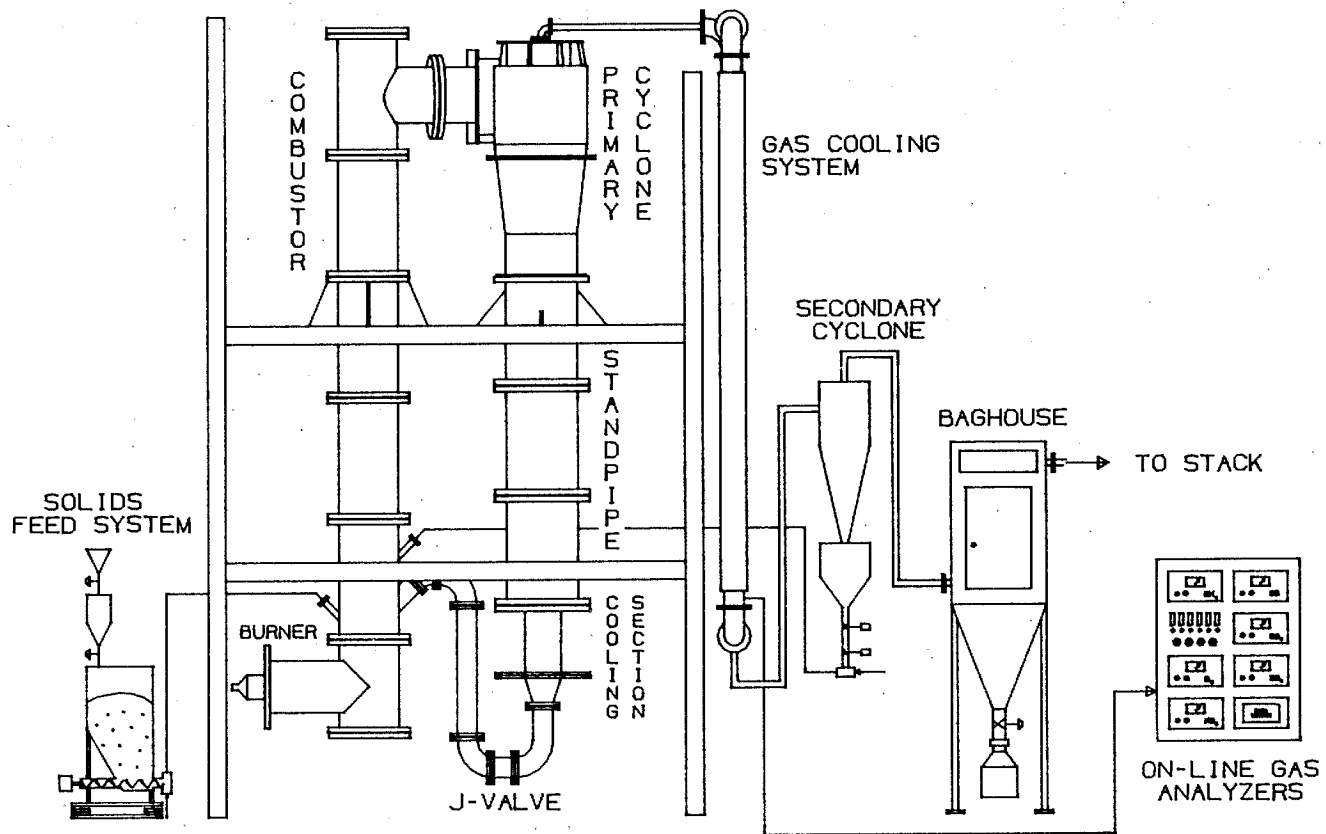


FIGURE 1: RPC CIRCULATING FLUIDIZED BED COMBUSTOR

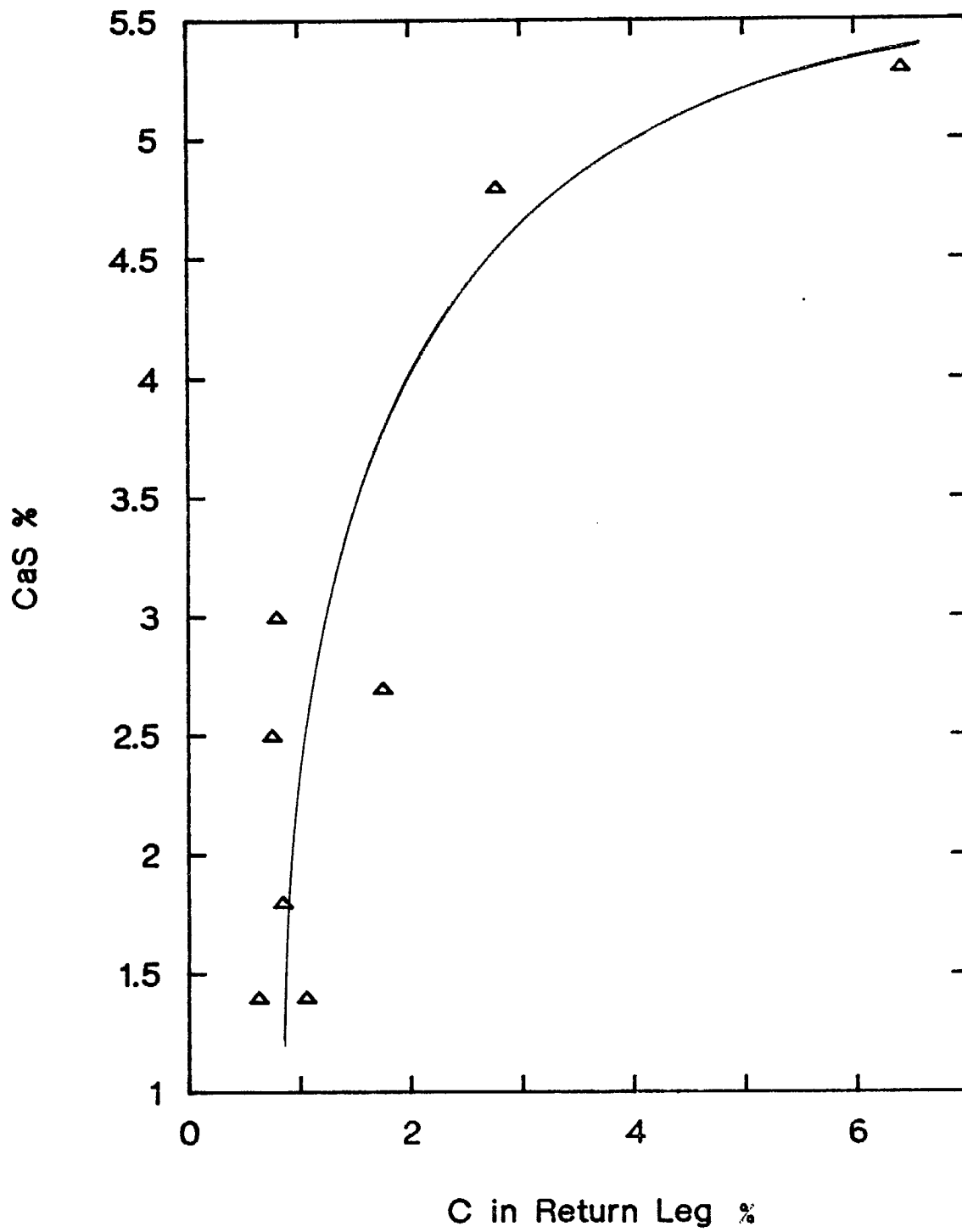


Fig.2 CaS Concentration vs Return Leg Carbon Content

Figure 3 Reaction Chemistry of  
CaS, CaSO<sub>4</sub>, and CaO  
in Combustors

