CALCITE IN COAL FROM THE QUINSAM MINE, BRITISH COLUMBIA, CANADA; ITS ORIGIN, DISTRIBUTION AND EFFECTS ON COAL UTILIZATION (92F/13,14)

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KEYWORDS: Quinsam mine, cleats, calcium oxide, calcite, calcite liberation, coal combustion, slagging, fouling, electrostatic precipitator, coal blending.

BACKGROUND

The Quinsam mine on Vancouver Island exports an excellent thermal coal with good heat value and a low ash concentration. However, the ash carries with it a higher than normal concentration of calcium oxide (CaO). This project investigates the origin and distribution of the CaO in the coal and looks at some of the ways it can effect the behaviour of the ash when the coal is burnt in a boiler.

A preliminary look at existing data and at some coal samples indicated that much of the CaO is in the coal as calcite and possibly other carbonates which coat the surfaces of cleats. If the calcite is not removed by washing then it adds CaO to that already in the ash. If the ash concentration is low then this addition of CaO can cause the concentration in the ash to rise markedly. The mineralogy of the ash ensures that it also contains some CaO. The concentration of this component of the CaO probably remains fairly constant from sample to sample and will not vary as the ash content changes. It therefore cannot be reduced by washing. The component of CaO originating from calcite can be removed from the coal if the calcite is liberated during washing. If it is not removed, the CaO concentration of the ash of the washed coal may be high and variable.

High concentrations of CaO in thermal coals can cause a number of changes in behaviour of the ash in coal boilers, such as lowering the melting temperature of the ash, increasing the ash adhesion to boiler walls and increasing the resistivity of fly ash. These changes are not necessarily bad but should be documented. Blending provides a way of ameliorating the extremes in the ash chemistry.

At present most of the coal at Quinsam is mined from the basal No. 1 seam, either from the 2-N underground mine or a number of surface pits. Knowing the distribution of calcite in No. 1 seam, both geographically and within the seam from hangingwall to footwall, may provide options for run-of-mine blending to reduce the CaO content of the raw coal.

QUINSAM COAL MINE

The Quinsam coal mine is located 20 kilometres west of the town of Campbell River on Vancouver Island (Figure 1). The mine has been in operation since 1987, initially as a small surface mine and now as a combined surface and underground operation. Present annual raw-coal production is about 650 000 tonnes.

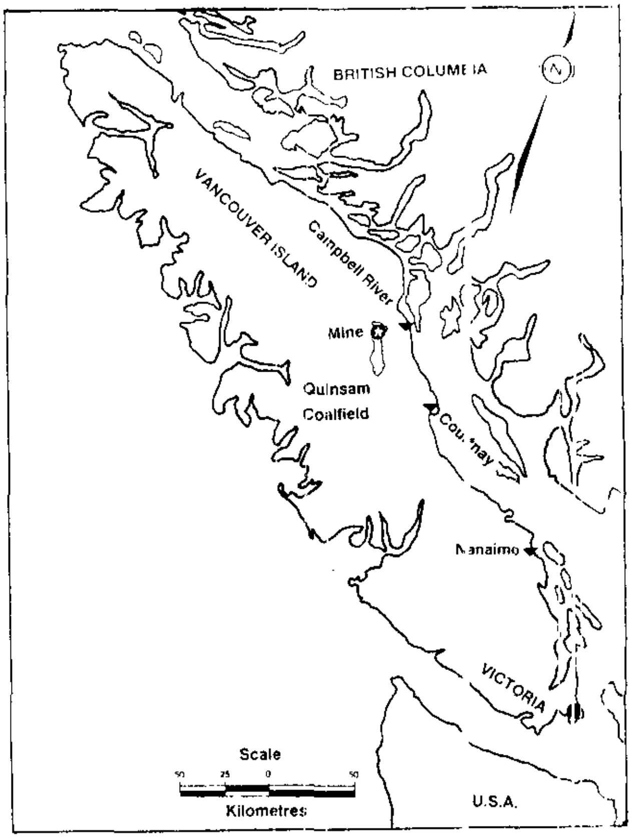

Figure 1. Location map of the Quinsam coal mine on Vancouver Island.

The coal seams at Quinsam are in the Comox Formation of the Upper Cretaceous Nanaimo Group (Kenyon *et al.*, 1991). The Comox Formation is divided into the basal conglomeratic Benson Member, which is overlain by the Cumberland and Dunsmuir members. Two seams outcrop in the Cumberland Member and two seams in the Dunsmuir Member. Most of the reserves are in the lowermost No. 1 seam in the Cumberland Member. This seam averages 2.3 metres in thickness and is sometimes overlain by a rider which averages 0.40 metre thick. It is mined underground and in surface pits. The overlying No. 2 seam averages 0.30 to 0.55 metre in thickness and is mined at surface in some pits. The No. 3 seam in the Dunsmuir Member averages 2.4 to 3.4 metres thick and is mined in surface pits. No. 4 seam is thin and is not mined. The stratigraphic separation from seam 1 to seam 3 is 30 to 60 metres.

CALCIUM OXIDE IN COAL

Calcium concentration is variously expressed as CaO% in the ash, CaO% in the total sample or as Ca in the total sample. If the calcium is mainly in mineral matter, its concentration on an ash basis will be independent of variations in the ash concentration. If it is mainly dispersed in the coal then its apparent concentration in the ash will increase as the amount of ash decreases.

Calcium oxide reported as a component of ash may actually be present in minerals that make up the mineral matter, as noncrystalline material associated with the coal or as minerals dispersed in the coal. Minerals found in the coal include carbonates such as calcite, dolomite, ankerite or siderite; minerals that make up the mineral matter include clays and feldspars. Minerals that may be associated with either mineral matter or coal include sulphates such as gypsum and phosphates such as apatite or gorceixite.

Calcium is introduced into the coal as part of the early coalification process, or later along cleats. Some calcium is initially extracted from sea water or ground water by the carboxylic acid groups (humic acid molecules). These molecules are destroyed by the coalification process and, at the same time, much of the interstitial water is expelled. Consequently as rank increases, CaO is released and moves through the coal with some of the interstitial water. During the early stages of coalification, siderite may form if conditions are anaerobic. This may be accompanied by dolomite if magnesium (indicating a marine influence) is present. Early forming carbonates may impregnate fusinite and semifusinite macerals because they have a structure and porosity which might not be present in vitrinite, which often does not have voids in its cell structure. During the second stage of coalification, calcite and ankerite crystallize, often on cleats (Stach *et al.*, 1975, p. 126). The CaO required to form these minerals comes in part from the coal but can be introduced from the surrounding rocks and penetrate the coal via the cleat system. Generally the reason for high concentrations of CaO in bituminous coals is the presence of calcite on cleats.

In general, the amount of CaO in coal decreases as the rank increases. Lindahl and Finkelman (1986) provide averages of 1.7% for lignites, 1.1% for sub-bituminous coals, 0.46% for bituminous coals and 0.1% CaO in total coal sample for anthracite. Raask (1985, p. 265) gives some data for low rank U.S. coals which show the same trend. Trends in British Columbia are similar. The Coal River lignite deposit has an average CaO content of 3.1%; the Hat Creek sub-bituminous deposit averages 0.29%; the Tuya River high-volatile B bituminous deposit averages 1.0 to 1.5%; the Telkwa high -volatile A bituminous deposit averages 1.0 to 1.5%; Kootenay medium-volatile deposits average 0.1 to 0.4% (with the exception of Byron Creek at 1.0%) and the Peace River medium-volatile deposits (Gates Formation) average 0.5 to 1.2% (Van der Flier-Keller and Goodarzi, 1992).

The exception to this trend is the Klappan anthracite deposit which averages about 1% CaO, noticably higher than the 0.1% average for anthracites. A plot of CaO in the total sample *versus* ash for Klappan data has a weak positive correlation, indicating that the CaO may, in part, be associated with fractures in the rock bands in the coal rather than with cleats. There is no correlation of CaO in the ash to ash content.

Whole-sample data for the Upper Cretaceous high-volatile bituminous coals on Vancouver Island average 1.65% CaO for 22 samples from the Comox Basin and 1.73% for 10 samples from the Nanaimo Basin to the south (Van der Flier-Keller and Dumais, 1988). The CaO content of the Wolf Mountain property (Perry, 1984) in the Nanaimo Basin is similar to the average for the basin. The average for the Chute Creek property in the Comox Basin is lower than the average for the Comox Basin.

The CaO content of 14 raw samples of No. 1 seam from the Quinsam mine averages 2.8% in the total sample (Matheson *et al.*, 1994) which is higher than the average for the Comox Basin. The averages for the No. 1 rider and overlying No. 2 seam are lower. The CaO contents in the ash do not correlate with the ash content or the amount of P_2O_5 in the ash (Table 1). In fact the CaO content does not have a positive correlation with any other oxide. Most of the CaO is therefore associated with a nonsilicate mineral, probably calcite, which is dispersed through the coal. In contrast, the medium-volatile bituminous coal seams in the lower part of the Mist Mountain Formation in southeast British Columbia generally have low concentrations of CaO, averaging 0.2% in the whole sample. Based on the correlations in Table 2, the CaO appears not to be associated with the ash and present in calcite, dolomite, siderite or phosphorus-bearing minerals that are dispersed thoughout the coal.

Whole samples of Upper Cretaceous coals on Vancouver Island have higher CaO contents than coals from southeast and northeast British Columbia. The higher concentrations are, in part, probably caused by calcite dispersed in the coal on cleats. The higher concentrations occur in both the Comox Formation in the Comox Basin and in the Extension and Protection formations in the Nanaimo Basin. In both basins it is the lowest seam which appears to have the highest CaO content (No. 1 seam in the Comox Basin and the Wellington seam in the Nanaimo Basin) and it is data from these seams that might be causing the high CaO% averages. In the Nanaimo Basin, data from seams other than the Wellington seam average 1% which is similar to the CaO concentration at Telkwa. The higher CaO in the lower seams may result from availability of CaO or because the seams have better cleat development.

TABLE 1

QUINSAM ASH OXIDE ANALYSES CORRELATION DIAGRAM

	ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5
ash	0.00	0.67	0.58	0.25	-0.78	0.12	0.71	0.76	-0.15
SiO_2		0.00	0.59	-0.10	-0.77	0.54	0.40	0.47	-0.09
Al_2O_3			0.00	-0.19	-0.52	-0.07	0.49	0.36	0.21
Fe_2O_3				0.00	-0.48	-0.21	0.27	0.66	0.12
CaO					0.00	-0.27	-0.59	-0.82	-0.15
MgO						0.00	0.16	-0.11	-0.11
Na_2O							0.00	0.56	-0.11
K_2O								0.00	0.06
P_2O_5									0.00

TABLE 2

SOUTHEAST BC ASH OXIDE ANALYSES CORRELATION DIAGRAM

	ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3
ash	0.00	0.77	0.20	-0.79	-0.74	-0.74	-0.13	-0.14	-0.62	-0.59
SiO_2		0.00	0.00	-0.96	-0.87	-0.94	-0.54	0.18	-0.24	-0.94
Al_2O_3			0.00	-0.19	-0.38	-0.19	0.49	-0.66	-0.75	0.00
Fe_2O_3				0.00	0.87	0.98	0.35	0.03	0.33	0.90
CaO					0.00	0.85	0.36	-0.04	0.57	0.88
MgO						0.00	0.31	0.10	0.27	0.90
Na_2O							0.00	-0.83	-0.34	0.58
K_2O								0.00	0.42	-0.26
P_2O_5									0.00	0.14

REGIONAL GEOLOGY, JOINTS AND ORIGIN OF CLEATS

Sediments often contain joints formed in response to regional tensional or compressive stress fields. Coal is also jointed but, because of its different rheology and maturation history, the joints generally have a different origin and are called cleats. Cleats usually form as orthogonal sets and are perpendicular to bedding. They are often parallel to, and sometimes connect with, regional joint sets in the surrounding sediments. The cleats are more closely spaced and generally do not exhibit the surface characteristics of shear joints. They probably form early in the maturation process, after the coal has become a fairly uniform, brittle solid (above a rank of sub-bituminous C) and while there is still a lot of compaction and water-loss induced shrinkage still to take place. Coal loses about 20% water by weight when the rank increases from sub-bituminous C to high-volatile B bituminous. This is equivalent to a 20% decrease in volume which is probably accompanied by additional compaction of the solid. Cleats form in the bright coal bands during coalification because bands which are ash poor and vitrinite rich are more brittle than the dull coal bands which are ash and inertinite rich (Gamson and Beamish, 1991).

The shrinkage often takes place in a subsiding basin which is experiencing regional stresses. These regional stresses, combined with shrinkage within the coal seam, produce two sets of tension cleats, one perpendicular to the basin axis and the other perpendicular to bedding and parallel the basin axis. The face cleats, which form first and are the through-going set are generally oriented at right angles to the basin axis, for example, the San Jaun Basin (Close and Mavor, 1991), the Mississippian and Pennsylvanian anthracite fields (Levine and Edmunds, 1993) and the Greater Green River Basin (Laubach *et al.*, 1993). Butt cleats, which terminate against the face cleats, are therefore generally oriented parallel the basin axis and often intersect bedding forming a line of intersection parallel the strike.

As the cleats are forming, water is being expelled from the coal and is channeled along the face cleats within the seams. Different lithotypes are more or less susceptible to shrinkage and water loss. At a rank of high-volatile bituminous, vitrinite can hold two to three times as much water as fusinite and therefore shrinks more during coalification. Water escaping from vitrain bands in the coal will tend to be trapped in the bands and move along face cleats, up the dip of the coal seam to the basin margins.

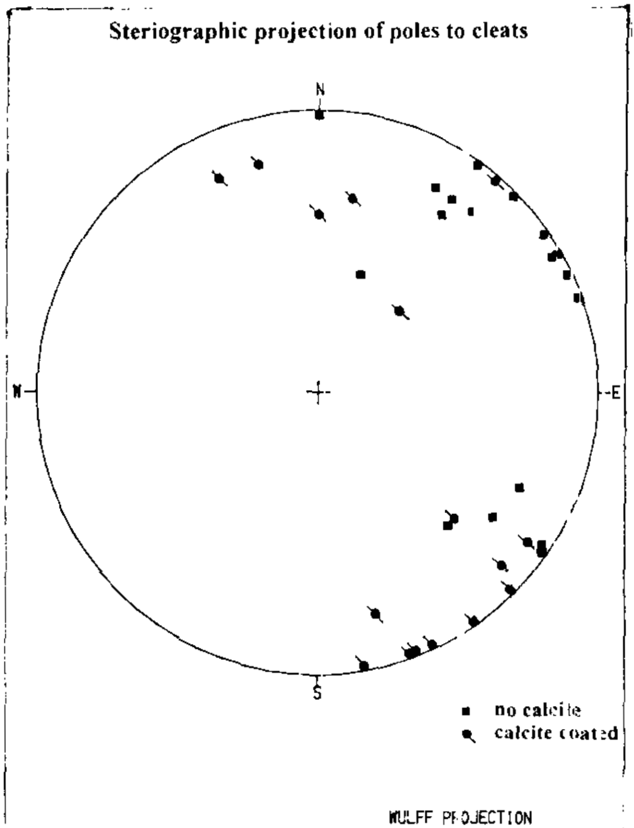

Figure 2. Sterionet plot of poles to cleats measured in this study.

Cleat orientations in No. 1 seam in the Quinsam mine were measured and the cleat coating, spacing and persistence noted. Generally the cleats are spaced between 0.5 to 10 centimetres apart and are persistent for up to 1 metre through the coal seams. Cleats are closer spaced and better developed in vitrain-rich coal. At most locations, two orthogonal set of cleats were measured, with, calcite coating often restricted to a single set. Cleat data are plotted as poles to surfaces (Figure 2). Calcite-coated cleats tend to strike east to southeast and cut across the trend of the bedding and basin axis. They appear to be the face cleats and are more dispersed than the second set of cleats that trend southeast and are parallel the basin axis.

The structure in the area has been discussed by Kenyon *et al.* (1991) and Gardner and Lehtinen (1992). Both papers describe early tensional faults trending easterly, which sometimes have calcite veins associated them. These faults are responsible for graben structures in the 2-N area and at surface are identified by low swampy ground. They also appear to act as channels for water into the underground mine. The calcite-coated cleat set is either related to these faults or to early stresses that formed the north to northwest-trending basin.

Gardner and Lehtinen (1992) identify a later period of pull-apart faulting that is largely restricted to the No. 1 seam zone. These faults parallel the strike of the beds and are down-dropped by a few metres on the down-dip side with respect to the regional bed-dip. The faults are gently dipping and consequently produce a barren zone up to 20 metres wide where they cut the coal seam. They probably represent ductile response of the incompetent No. 1 seam to buckling and down-warping of the sedimentary succession. A later period of northeast to southwest compression is described by Kenyon *et al.* (1991); it produced some folds and southwest-verging thrusts. They also identified a period of tear faulting that is probably post Late Eocene. These faults trend northeast to east and are assumed to be unrelated to any joints.

It is proposed that both sets of cleats formed early in the tectonic history, after the coal had reached a rank of more than sub-bituminous C. The east-trending face cleats formed first and remained open, but later east-west compression tended to close the southeast- trending butt cleats. Calcite could therefore have been introduced into face cleats at any time. Early calcite could originate from dewatering of the coal seam and late calcite from present day ground water movement.

CALCITE IN QUINSAM COALS

When visually estimating the amount of calcite in the coal it should be remembered that, because of the density difference between coal and calcite, the volume percent of calcite in the coal will be 53% less than the weight percent. The presence of calcite in Quinsam No. 1 seam was confirmed using simple field tests. The coating effervesces in cold dilute hydrochloric acid and is therefore probably mostly calcite and unlikely to contain much dolomite, siderite or ankerite. Analyses of sulphur in samples of fresh No. 1 seam indicate that there is very little sulphate and therefore very little calcium sulphate (gypsum) in the seam. Calcite was also stained using alizarin red S solution after etching with 10% hydrochloric acid. The stain confirmed the white joint-filling material was calcite. Calcite also fluoresces under short wave ultraviolet light. It was found that the calcite fluoresced a dull white when well exposed. This test was useful on individual samples and may be applicable in an open pit at night, unfortunately it could not be tested underground because of safety requirements and limestone dusting in the underground mine.

The calcite occurs in three general forms. Most is on the surfaces of cleats which are perpendicular to bedding (Photo 1); some occurs in desiccation fractures restricted to vitrain-rich bands1 to 5 centimetres thick (Photo 2).

Photo 1. Calcite on cleats in a sample of Quinsam coal.

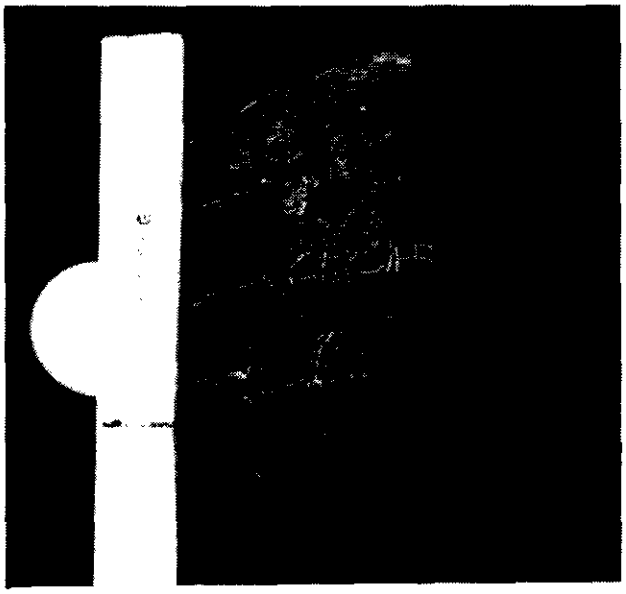

Photo 2. Calcite-filled crackle zone in a sample of Quinsam coal.

Calcite also occurs on crosscutting shear fractures with minor dilation (Photo 3). Calcite-coated cleats were observed in the coal underground in the 2-N area and at surface in the 4-S area (Figure 3). Calcite occurs on cleats as thin grey or white smears; it is discontinuous and does not form thicker veinlets. The cleats are perpendicular to bedding, 0.5 to 10 centimetres apart and usually terminate against high-ash or inertinite-rich bands. If the cleat traverses the ash band then that part of the surface tends not to be calcite coated. The calcite smearing is less than 1 millimetre thick, not striated, and under the microscope appears to be fractured into 1 *millimere or smaller rectangular fragments. Because the* calcite seems to be pervasive on at least one set of cleats, and the cleats generally do not connect with joints in the interburden, it appears that the calcite has moved parallel to bedding through the seam, at least in part. The calcite that fills discontinuous microfratures within thin vitrain bands may have been deposited earlier than the cleat calcite, and the calcite on crosscutting fractures was probably deposited last.

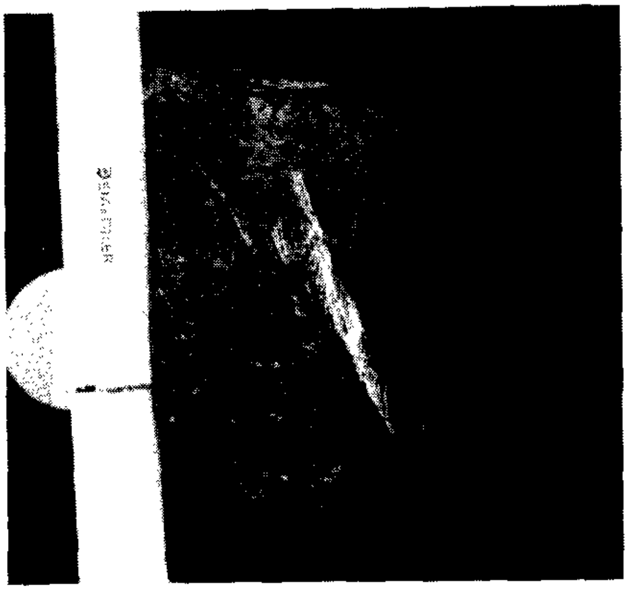

Photo 3. Calcite-filled fracture in a sample of Quinsam coal.

MEASUREMENT AND IDENTIFICATION TECHNIQUES FOR CaO AND CALCITE

The CaO content of a sample is measured as a component of the ash which is left after the coal is burnt off in the analysis process. The ashing process will not volatilize calcium in any form so that it remains in the ash residue. The calcium in the ash is usually measured by atomic adsorption spectroscopy and the results reported as CaO%.

For coals in which most of the CaO is from calcite, there might be a test that requires simpler equipment. The approach, used in this study, involves dissolving and removing the calcite from the sample with hydrochloric acid and then weighing either the leached sample or the precipitate retrieved after drying the acid leachate. A coal sample *with 1% calcite contains* 0.56% CaO and 0.44% CO_2. Forty grams of this sample contains 0.004 moles of CaO. This requires at least 0.008 moles of HCl or 8 millilitres of 1 molar HCl to convert the calcite to CO_2 and $CaCl_2$. Sufficient 1 molar HCl was added to samples to dissolve the calcite and the acid was then filtered off the coal sample and the sample dried. The sample weight after drying should indicate the amount of calcite removed. Unfortunately the drying process also removes water from the coal so that the leached sample has less water than the sample prior to leaching. This effect is particularly apparent for low rank coals that have variable and high as-received water contents. The HCl *extracted from the leached sample was evaporated to* dryness and the residue weighed. If the leaching only removes calcite and the precipitate is calcium chloride then it is possible to calculate the calcite concentration in the sample. Some uncertainty is introduced by the fact that the acid may dissolve some of the pyrite and other carbonates and iron and magnesium chlorides may also be precipitated.

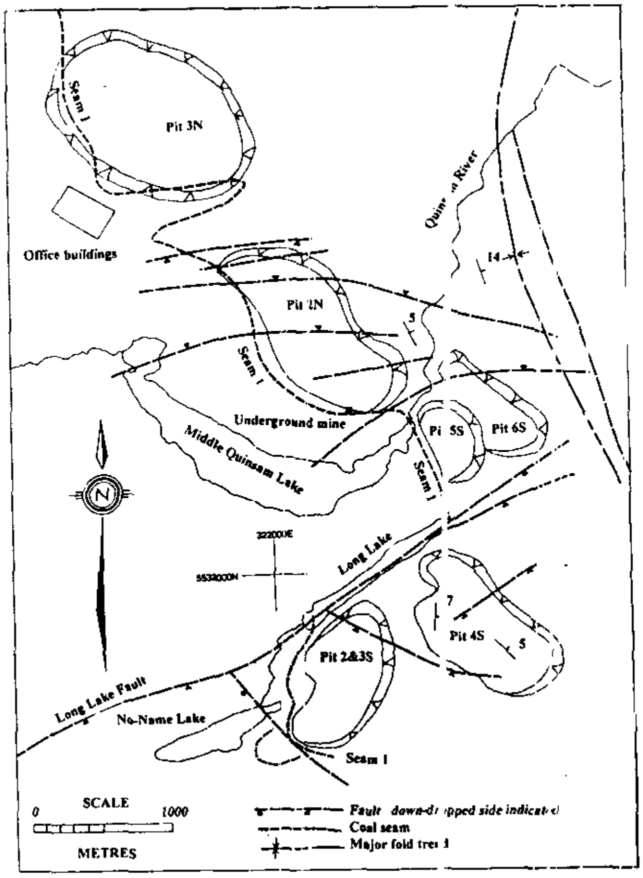

Figure 3. Mine geology and infrastructure showing location of pits and underground mine.

SAMPLING AND ANALYTICAL RESULTS

Thirteen locations were sampled in the underground mine, two locations in the No. 2 South surface pit and two drill holes from the 1992 exploration program (D10 and D13). In addition some drill-hole data from the 1992 Quinsam mine assessment report were used. All the data *are in Table 3; sample sites with the exception of D21* and D25 are located on Figure 4 and coordinates are in Table 4. These two drill holes are collared to the east of the area covered by Figure 4. A total of 30 samples were analyzed in the study.

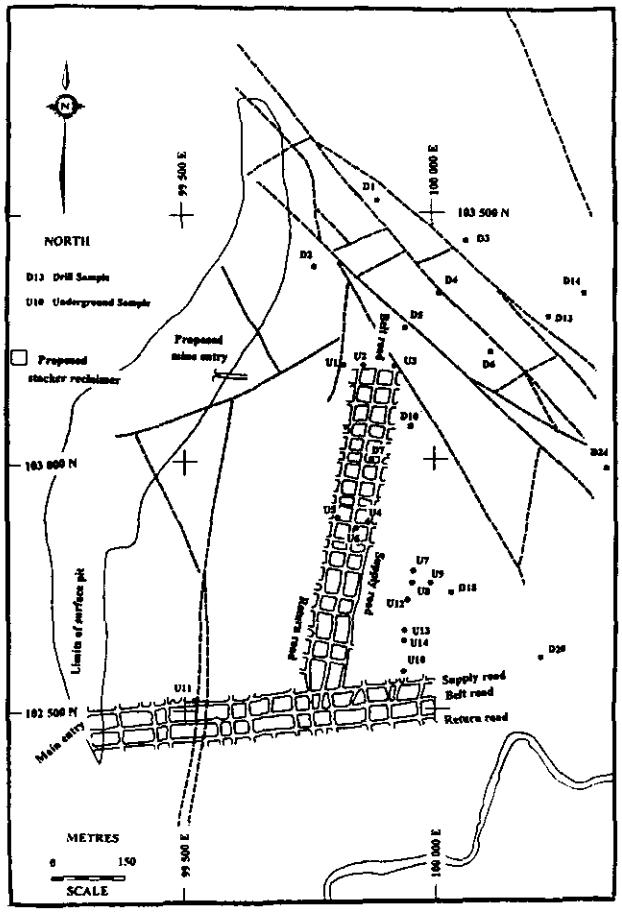

Figure 4. Location of underground samples in 2N underground mine.

The underground room-and-pillar mine extracts the top two thirds of the No. 1 seam and sometimes part of the overlying mudstone split and rider seam. The remaining footwall coal is sometimes recovered when the pillars are removed before sections of the mine are allowed to cave. Sampling is complicated by the fact that the coal is hard and not well cleated, and coal faces are dusted with limestone to reduce fire hazards. Generally about 1 metre of hangingwall coal was taken as the first sample, and as much of the remaining seam as was exposed as an additional sample. A vertical strip down the coal face, about 10 to 20 centimetres wide was cleaned off and samples collected as large fragments across the face. From 1 to 5 kilograms of coal was taken for each sample. Samples were washed at surface to remove any trace of the limestone dust.

Samples were crushed and split and some chemistry performed in the mine laboratory facility by the author, with the cooperation of Quinsam personnel. One of the splits was leached with hydrochloric acid. Splits of the raw sample, leached sample and dried precipitate from the leached sample were sent to a commercial laboratory for analysis. Raw and leached samples were analyzed for CaO% in the ash and total sulphur. Some samples of the calcium chloride precipitate were analyzed for CaO, Fe_2O_3 and MgO, and some of the coal samples were also analyzed for sulphur forms. The data are presented in Table 3.

The amount of CaO originating from calcite in the ash is calculated by subtracting the leached ash CaO% concentration from the initial ash CaO% concentration. Based on the amount of ash, this concentration can be expressed in terms of the whole sample or as a concentration in the coal-only part of the sample. The CaO% from calcite in the whole samples ranges from 1.6% to 4.22%. This is equivalent to a range of 2.3% to 7.2% mass of calcite or 1.2% to 4.1% volume of calcite in the whole sample.

The CaO content in the ash of the leached samples ranges from 1.17% to 16.44%. Two of the samples have distinctly higher concentrations of CaO than the rest (U1-1 and D13-1, Table 3). Either these samples contain a carbonate that is not leached by cold hydrochloric acid or some of the calcite was not removed. X-ray diffraction analyses of the sink ash from splits of these two samples indicated that the ash is composed of over 90% calcite with minor kaolinite and quartz. This indicates that some of the calcite was not leached. To check this, a plot of CaO in the ash before leaching *versus* CaO in the ash after leaching (Figure 5) was constructed. The data have a positive correlation factor and a best-fit line through the data indicates that the leached and unleached CaO values are the same at 0.4%. The unleached CaO value cannot be lower than the leached value, so 0.4% is probably the best estimate of the average CaO in the ash, not attributable to calcite. The increment of CaO in leached samples above 0.4% is probably calcite that was not dissolved by the acid.

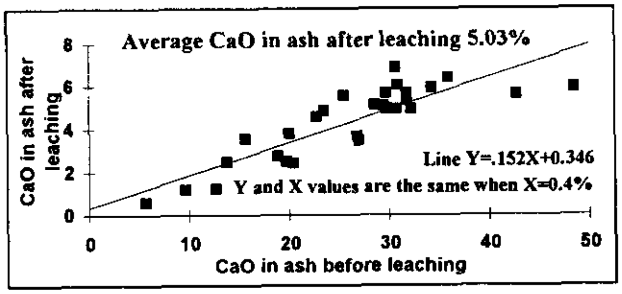

Figure 5. Effects of leaching CaO from ash.

It is also possible that the acid leach dissolved other carbonates. To check this, two precipitate samples with CaO contents of 29.5% and 38.9% were analyzed for MgO and Fe_2O_3. There was less than 0.3% Fe_2O_3 or MgO in the precipitates, indicating very little solution of dolomite, siderite or ankerite.

The possible solution of pyrite by the hydrochloric acid was checked by analyzing the total sulphur in the fresh and leached samples (Figure 6). The data plot close to a line with a slope of 1, indicating no loss of sulphur in the leached samples. A slope of less than 1 would indicate acid leaching of pyrite as pyritic sulphur makes up a component of the total sulphur. A plot of total sulphur *versus* pyritic sulphur (Figure 7) indicates that, for the underground data from this study, the amount of pyrite in a sample can be estimated using the linear relationship:

pyritic sulphur = 0.253 x total S% - 0.0465

The remaining sulphur is mostly organic. However surface data from Matheson *et al.* (1994), also in Figure

7, indicate that a larger proportion of the total sulphur is in pyrite. A plot of CaO from calcite in total sample *versus* pyritic sulphur (Figure 8) indicates a weak tendency for high pyritic samples to also have low calcite contents, but there is no clear relationship.

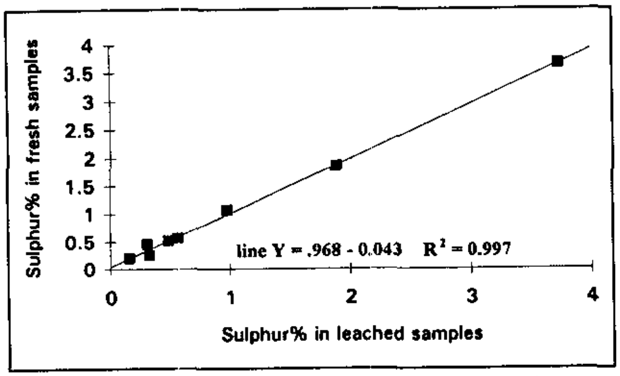

Figure 6. Total sulphur in fresh and leached samples.

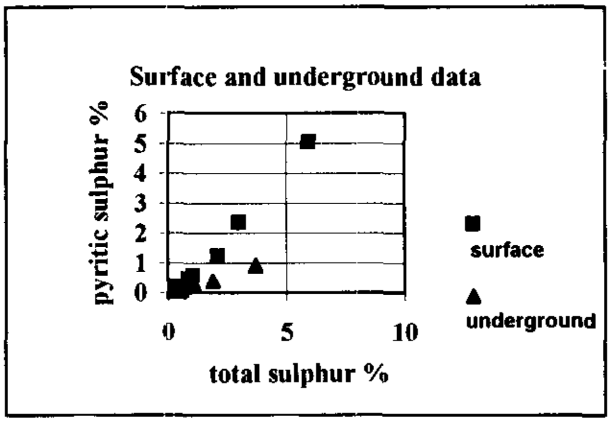

Figure 7. Relationship of total sulphur to pyritic sulphur.

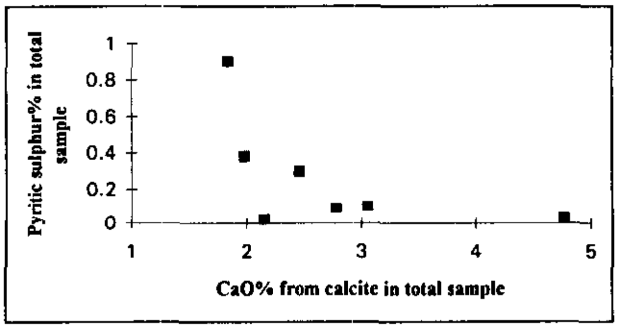

Figure 8. Pyritic sulphur *versus* CaO% from calcite in the total sample.

In most cases the acid-leach solution was rinsed off the coal sample through a filter and dried. The weight of precipitate divided by the sample weight should correlate with the amount of CaO derived from calcite in the total sample. In fact, if the precipitate is $CaCl_2$ then it is equivalent to 50.53% CaO. It should be possible to use the weight of precipitate to calculate the amount of calcite in the sample and, if there is a constant non-calcite-derived CaO concentration in the ash of 0.4%, it should also be possible to estimate CaO content of the total sample. A plot of weight of precipitate expressed as CaO in the total sample(X) *versus* CaO in the total sample minus 0.4%(Y) produces a line:

$$Y = 0.869 + 0.585 \qquad R^2 = 0.89 \text{ (Figure 9)}$$

The line should have a slope of 1 and a zero intercept. It does not because not all the calcite was dissolved and so the precipitate weights are low by an amount dependent on the amount of calcite in the original sample.

The line in Figure 5 can be used to correct the precipitate weight and if this is done then the line:

$$Y = 1.17\,X - 0.273 \qquad R^2 = 0.91$$

is generated (Figure 10).

The data indicate that it might be possible to use the precipitate weight to estimate the total CaO in the sample. Based on the data in Figure 5 the average error in predicting total CaO using the corrected precipitate weight is 10% of the value and, at a one standard deviation, errors ranging form 2% to 16% can be expected. If the chemical procedure is improved so that all the calcite is dissolved, then better predictability could be achieved.

The mineral matter in No. 1 seam is somewhat unique in that it appears to have a very low content of free quartz. Because of the high carbonate content of some of the ash (up to 50% calcite), the mineral matter may lose up to 40% of its weight on ashing. This means that a sample with 16% mineral matter, containing a high calcite content, will report as about 10% ash and the coal will appear to have an unusually low heat value based on the 10% ash content.

REGIONAL DISTRIBUTION OF CALCITE WITHIN ONE SEAM

The data were analyzed to see if calcite distribution is systematic. Generally, more than one sample was collected from each site. The variation in CaO% for samples from a single site is almost as large as the variation between sample sites. A set of five channel samples, spaced 5 metres apart in the underground mine, also showed a wide variation of CaO content (S. Gardner, Quinsam mine, personel communication 1994). There does not seem to be a correlation of CaO% with position in the seam. Hangingwall samples do not consistently have higher CaO concentrations than mid-seam samples. All the samples at a single site were averaged to provide the best estimate of the CaO content for the full seam.

A variogram for total CaO% *versus* distance indicates poor if any significant spatial trends in the data. Despite this, simple contour maps were produced for total CaO% in the total sample (Figure 11) and CaO derived from calcite expressed as percent of the coal-only component of the total sample (Figure 12). Because the calcite is mostly on cleats that are restricted to the coal, it was felt that a contour map of CaO in the coal only might reveal regional trends. The CaO in the ash was corrected to CaO in coal-only using:

TABLE 3. ANALYTICAL DATA FOR UNDERGROUND SURFACE AND DRILL-HOLE SAMPLES

sample	thickness	wt smple	H_2O	Ash%	CaO_t%	CaO_r%	total S%	pyrtc S%	SO_4%	wt ppt
U1-1	HW-2.0M		1.53	6.81	40.45	16.44	0.52			
U2-1	HW-.70M	39.466	1.45	9.09	34.28	5.9	0.57			2.016
U2-2	.70-1.9M	40.006	1.35	9.6	31.77	5.65	0.29			1.725
U3-1	HW-1.0M	38.841	1.37	9.98	29.79	4.94	0.53			2.046
U3-2	1.0-1.9M	40.181	1.27	11.16	20.01	3.78	0.27			1.438
U4-1	HW-.80M	42.405	1.4	9.81	25.5	5.54	1.09	0.3	0.13	2.009
U4-2	.80-1.50M	47.553	1.52	7.86	23.5	4.84	0.26			1.562
U5-1	HW-.80M	43.705	1.41	9.75	22.8	4.56	0.36			1.513
U6-1	HW-.40M	43.141	1.35	9.97	29.74	5.65	0.57			2.456
U7-1	1.5M-FW	37.292	1.16	19	9.63	1.17	0.19			1.258
U8-1	HW-1.55M	38.561	0.89	7.89	28.56	5.1	0.33			1.612
U9-1	HW-.40M	40.677	0.91	13.06	19.68	2.48	0.43			2.333
U10-1	RDR .45M	41.265	1.42	14.82	13.77	2.46	1.88	0.38	0.21	1.419
U10-2	HW-.40M	43.783	1.43	9.14	30.87	6.01	0.52	0.09	0.03	2.461
U10-3	.40-1.20M	38.821	1.42	9.93	48.45	5.9	0.46	0.03	0.01	3.851
U11-1	HW-.60M	42.965	1.52	12.06	15.61	3.54	3.71	0.9	0.25	1.026
U12-1	HW-.50M	42.121	1.42	10.08	30.76	4.9	0.57	0.1	0.02	2.511
U12-2	.50-1.4M	47.872	1.43	7.12	30.67	6.86	0.25	0.02	<0.01	2.093
U13-1	HW-.60M	43.516	1.4	11.05	42.75	5.59	0.65			3.847
U13-2	.60-1.20M	49.195	1.37	7.92	35.92	6.38	0.28			1.918
U13-3	RDR .2-FW	41.285	0.92	31	12.7	1.21	2.17			2.652
D10-1	67.8-69.2M	41.502	0.96	11.4	29.5	5.05	0.25			2.301
D10-2	69.2-70.1M	46.275	0.92	10.6	18.82	2.73	0.22			1.496
D13-1	96.7-97.3M	41.056	1.02	5.06	38.86	13.88				1.219
D13-2	97.3-98.6M	43.194	1.03	9.28	32.2	4.9	0.29			2.299
D13-3	98.6-100.5M	41.377	1.01	9.42	31.81	5.33	0.27			1.975
S1-1	HW-1.2M	39.656	1.19	8.08	26.93	3.45	0.68			1.44
S1-2	1.20-1.5M	42.086	1.11	30.38	5.65	0.58	0.65			1.061
S1-3	1.55-2.55M	41.829	1.16	13.42	20.37	2.39	0.57			2.003
S2-1	HW-2.2M	40.704	1.28	9.84	26.85	3.65	0.98			1.886

CaO_t=total CaO in ash CaO_r=CaO in ash after leaching

S%= pyritic sulphur in total sample wt ppt= weight of precipitate from sample acid leach solution

CaO in coal = CaO in ash x ash /(100-mineral matter)

mineral matter =(ash x (1-(CaO-0.4) in ash/100) x1.08

An attempt is made to calculate the actual mineral matter, not a combination of mineral matter plus CaO reporting to the mineral matter. For this reason, the amount of CaO (minus 0.4%) is subtracted from the amount of ash and then the amount of ash multiplied by a constant to account for the loss of weight experienced when mineral matter composed of quartz and kaolinite is ashed.

The CaO content in coal varies from 2.4 to 4.4%. When the data are averaged on 100 by 100-metre blocks, and contoured, there is a tendency for CaO to increase to the northeast and southeast of the area covered by Figure 12.

Data were also provided by Quinsam staff for areas adjacent to the 2N underground mine and the same pattern of variability was observed. In the S5 area, 500 metres south of the 2N underground mine, two holes 200 metres apart have CaO contents of 6.15% and 1.87% in the coal. The 3N area, 1 kilometre north of the 2N underground mine, can be divided into a higher CaO area to the northeast and a lower CaO area to the southwest, based on five samples.

A preliminary correlation matrix was constructed using drill-core data and containing seam thickness, separation from rider seam, thickness of in-seam split and CaO content of coal. It was found that there is a weak correlation of CaO to in-seam split thickness. It would be interesting to continue this analysis with more data and more variables in the matrix. In a broad sense the CaO content does not seem to be related to distance from faults, although on a local scale, it may be. If CaO content is controlled by cleat development, then calcite content may be related to variable compaction effects caused by changes in the amount of sand in the lithological section above or below the coal seam.

SEPARATION OF CALCITE

A detailed study was undertaken by CANMET (Mikhail *et al.*, 1993) to investigate the washing characteristics of Quinsam coal, with particular reference to the CaO content of various fractions. Some of the data were made available to be used in the present study.

Before the content of calcite in the coal can be calculated, the amount of CaO originating from the ash must be known and subtracted from the total CaO content. If the CaO content is assumed to be constant for the ash in different sized fragments and in different

TABLE 4. SAMPLE LOCATIONS AND AVERAGE CaO% DATA

sample	easting	northing	CaO_cl%	CaO_tot%
U1	99816	103191	2.88	2.75
U2	99859	103186	3.3	3.07
U3	99916	103180	2.87	2.62
U4	99868	102872	2.38	2.2
U5	99806	102881	2.42	2.22
U6	99840	102866	3.21	2.97
U7	99954	102775	2.25	1.83
U8	99954	102760	2.4	2.25
U9	99992	102754	2.9	2.57
U10	99938	102581	4.4	3.95
U11	99522	102518	2.12	1.88
U12	99950	102718	2.68	2.51
U13	99942	102655	4.04	3.78
U14	99937	102640	ND	ND
D92-10	99954	103067	2.7	2.83
D92-13	100238	103296	2.32	2.84
D92-1	99883	103524	4.21	3.78
D92-2	99763	103396	3.27	2.96
D92-3	100062	103440	2.95	2.48
D92-4	100012	103344	3.17	2.65
D92-5	99940	103266	3.77	3.15
D92-6	100115	103215	3.34	2.79
D92-7	99868	102999	3.46	2.91
D92-14	100306	103336	3.17	2.65
D92-20	100216	102600	4.08	3.4
D92-21	100502	103032	3.08	2.53
D92-24	100356	102970	3.40	2.86
D92-18	100031	102738	4.12	3.09
D92-25	100507	103473	3.20	2.65
S1	97900	101650	2.65	2.34
S2	97700	101150	2.86	2.64

CaO tot% = total CaO in total sample
CaO cl% = CaO in coal part of sample only

specific gravity splits, then the calcite content of the total sample can be calculated.

If the calcite is associated with coal and, when liberated, forms small fragments, then the CaO contents of the 2.17 S.G. sinks for the coarse fragments will be mainly rock-split fragments with very little calcite. The CaO content of the 100-25, 25-10 and 10-0.5-millimetre-sized sinks (S.G. >2.17) are 0.81%, 0.51% and 1.36%. It is therefore safe to assume that the CaO content of the ash averages less than 1% and any CaO in excess of this amount is probably present as calcite. An ash-based CaO content of less than 1% for the single washability sample agrees with the 0.4% value determined from the 30 acid-leached samples.

The amount of calcite in the coal is calculated by subtracting 1% from the total CaO ash content and assigning the excess to calcite in the coal. The amount of calcite in the original sample can be determined by calculating the calcite in each size increment and weighting them together. This provides an average concentration of 3.6%, which is less than the calcite concentration in the 100-25-millimetre size fragments (4.57%). It is unlikely that these particles experienced any liberation of calcite and the calcite content of the other size fractions must average less than 3.6 % to ensure the overall average of 3.6%. A summary of calcite distribution by size and specific gravity, calculated assuming a constant 1% CaO from non-calcite sources, is presented in Table 5. The same information is displayed diagramatically in Figure 13

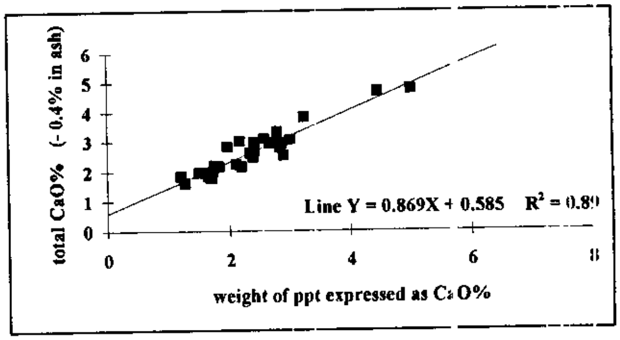

Figure 9. CaO% from calcite total sample *versus* CaO% in precipitate.

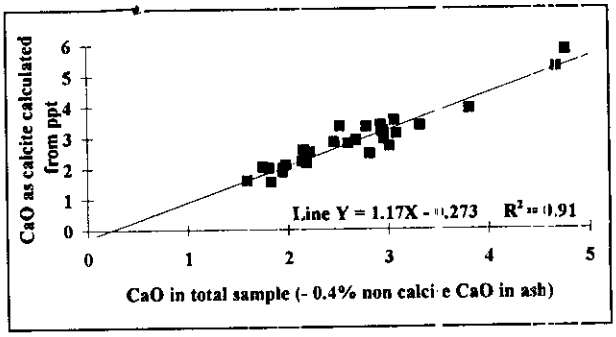

Figure 10. CaO% from calcite in total sample *versus* CaO% in precipitate, corrected for partial solution of calcite.

The amount of calcite liberated by crushing the raw coal can be estimated by subtracting the calcite content in the sizes 25-10 and 10-0.5-millimetres from an estimated average starting calcite content. This provides a minimum liberation of about 20%. The calcite content of the 0.5-0.15 and 0.15-0-millimetre sizes is increased by the addition of liberated and broken calcite fragments derived from the coarser sizes. The liberated calcite in the finer sizes may be all of the calcite in the size fractions or just that component above the average If all the calcite in the 0.15-0-millimetre size range is liberated together with half in the 0.5-.15-millimetre range then this provides an estimate of about 20% liberated calcite which agrees with the amount released from the coarser size fractions. It appears that the crushing process has liberated about 20% of the calcite in the raw sample. The 100-25-millimetres size fraction contains about 30% of the total calcite in the sample. The concentrations of calcite in the size ranges 25-10 and 10-0.5-millimetres are about two thirds the average indicating about a 30% liberation of calcite in these size fractions. Based on these numbers, crushing the whole sample to a 25-millimetre

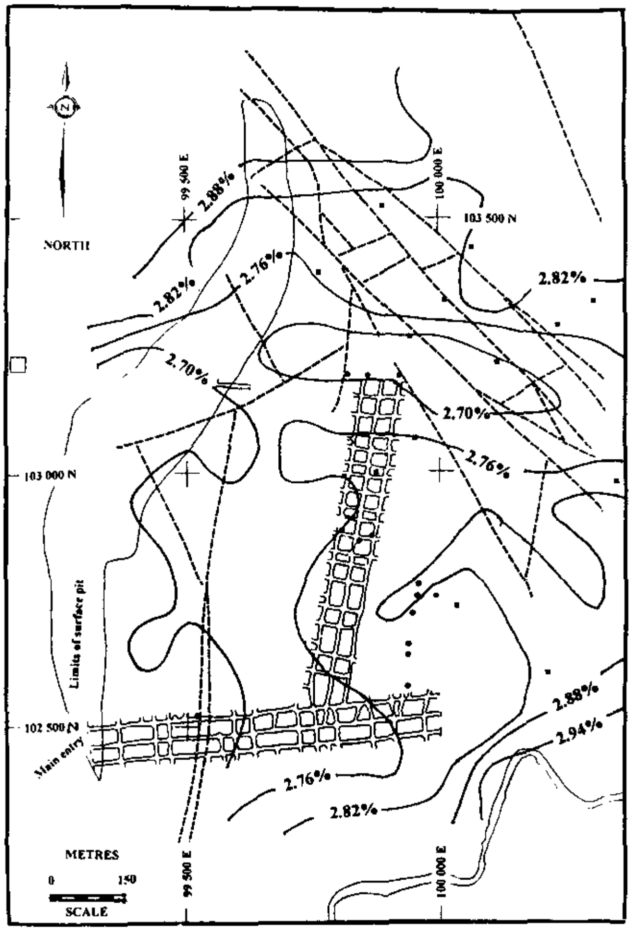

Figure 11. Map of 2N underground mine showing contours of total CaO% in total sample.

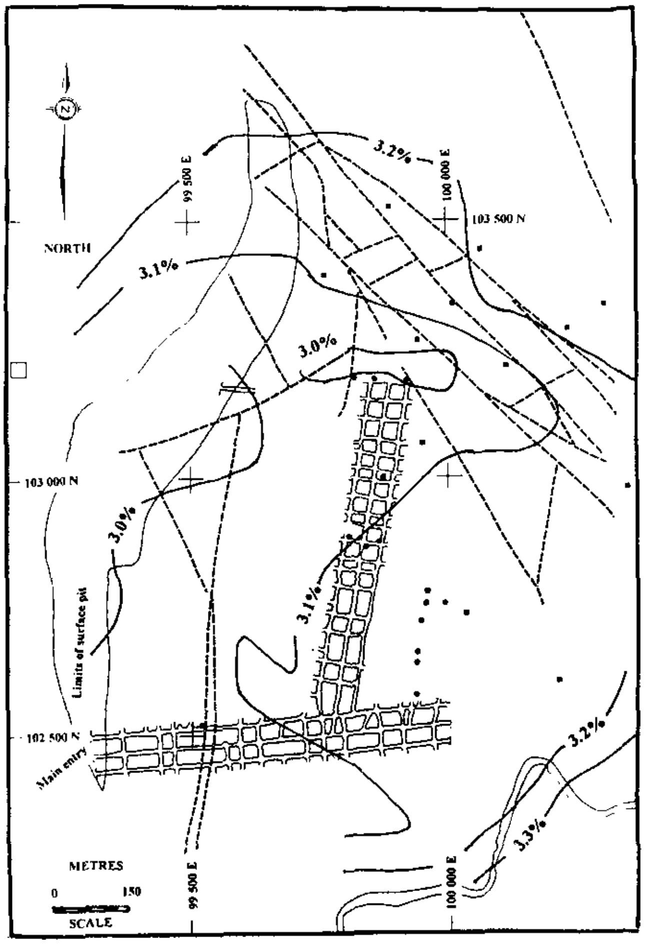

Figure 12. Map of 2N underground mine showing contours of calcite in coal-only part of sample.

top size would probably increase the calcite liberation from 20% to 30%.

It is possible to estimate the new particle-size distribution achieved by crushing the whole sample to a top size of 25 millimetres by plotting the existing size distribution on Rosin Rammler paper and then moving the line to the left to predict the new top size of 25-millimetres. This type of analysis indicates that the amount of minus 0.15-millimetre material will increase by at least 10%. An alternative approach in the plant, which would produce less -0.15-millimetre material, would be to screen and recrush only the 100-25-millimetre fraction. This should produce the same increase in calcite liberation without a large increase in the amount of fines.

Based on the above data, there is little if any liberated calcite in the 100-25, 25-10 and 10-.5-millimetre size fractions. Washing of these fractions will remove calcite as calcite-plus-coal particles, but will also reduce the ash and concentrate the remaining calcite in the remaining ash. The calculated calcite content of the >2.17 S.G. sinks in these sizes is low. This also indicates that there is very little liberated calcite. Most of the calcite is in the 1.5 to 1.7 S.G. splits and based on the amount of calcite and the specific gravity of the separating liquid, the specific gravity of the coal associated with the calcite has to be 1.35 in the 100-25 and 25-10-millimetre size fractions and 1.6 in the 10-0.5-millimetre size fraction. Obviously the calcite is associated with low ash coal in these size fractions. Most of the calcite liberated and fragmented from the coarse size fractions reports to the finest fraction where the >2.17 S.G. sinks contain 21% calcite.

The calcite is not easily liberated from coal particles but when it is, it breaks into particles less than 0.5 millimetres in size. Calcite can be removed as coal-plus-calcite particles from the size fractions greater than 0.5 millimetre by washing at specific gravity's ranging from 1.5 to 1.7. Calcite on cleats in hand samples appears to break off easily and it is surprising that it does not completely separate more easily from the coal. It is possible that it is not restricted to the cleats and some is dispersed through the coal.

ASH CHEMISTRY, CALCIUM OXIDE CONTENT AND THERMAL COAL UTILIZATION

Ideally an operator would like to burn ash-free coal in a power plant. In fact, with normal coal cleaning, about 5 to 15 % of the material introduced into the boiler

TABLE 5. CALCITE DISTRIBUTION BY SIZE AND SPECIFIC GRAVITY

Calcite calculated assuming 1% CaO not from calcite

RAW DATA

size mm	wt fraction	ash%	CaO% ash	wt calcite	volume calcite
100-25	23.49	32.75	8.82	4.57	2.41
25-10	24.25	32.63	4.87	2.25	1.17
10-0.5	40.21	31.28	5.88	2.72	1.42
0.5-0.15	4.51	21.37	15	5.36	2.84
0.15-0	7.54	42.29	12.6	8.79	4.74

Average calcite in sample =3.62% based on 1% CaO in ash minerals

WASH DATA

size in mm	100-25		25-10		10-0.5		0.5-0.15	
S.G.	ash%	wt calcite	ash%	wt calcite	ash%	wt calcite	ash%	wt calcite
1-1.3	6.04	0.9	3.98	0.95	4.78	13.8	4.22	0.495
1.3-1.35	6.39	2.63	5.72	2	5.45	13	6.15	0.604
1.35-1.4	10.52	6.5	9.87	5.6	9.92	15.9	7.74	0.86
1.4-1.45	14.43	9.7	15.03	6.4	14.32	18	10.36	1.02
1.45-1.5	17.66	12.7	18.73	10	18.4	22.6	15.12	1.49
1.5-1.6	21.8	16.3	24.16	13.9	23.43	23.6	19.43	2.13
1.6-1.7	30.75	9.7	33.7	10.5	30.72	20.4	28.15	3.13
1.7-1.8	44.44	9.9	45.25	5.8	38.91	20.3	36.79	5.42
1.8-2.0	51.18	3.3	53.85	1	51.83	11	47.89	8.12
2.0-2.17	65.85	0.5	66.84	2.7	61.46	10.6	58.93	11.9
2.17-2.5	80.46	0	80.94	-0.5	81.42	1	79.3	21.3

wt calcite = weight of calcite in sample

is ash. It must be collected either as small particles (fly ash), as dry-bottom deposits or as liquid slag, and removed. Many modern boilers use pulverized coal and are designed to handle ash as dry deposits most of which (80%) is collected as fly ash in electrostatic precipitators. The rest is removed as dry-bottom deposits via hoppers at the base of the combustion chamber. The operator is looking for an ash that will:

- Not produce a slag (melt at operating conditions; slagging problems).
- Not produce dry, sticky deposits in the boiler that may be difficult to dislodge and collect in the bottom hoppers (adhesion problems).
- Not produce deposits on the water tubes that corrode the metal (corrosion problems).
- Not contain refractory mineral fragments that will abrade metal surfaces (erosion problems).
- Be easy to collect as a fly ash in the electrostatic precipitators (favourable ash electrical resistivity)

In part, these properties are related to the size, segregation and form of the mineral fragments that enter the boiler with the coal. They can also be predicted, to some extent, using average ash chemistry.

The oxide chemistry of the inherent mineral matter in a particular seam is typically fairly constant. Variations are caused by variable additions of minerals associated with the coal, for example calcite, other carbonates, phosphates and pyrite. The amount of sulphur in the clean coal is closely monitored so that the main variations in clean-coal ash chemistry will be related to variations in CaO, Fe_2O_3 and MgO content. The main variant in the ash chemistry of Quinsam coal is CaO derived from calcite.

It is important to understand how variation in the content of these oxides changes the important ash properties of slagging, adhesion, corrosion, abrasion and ash resistivity, and effects the operation of the most commonly used pulverized-coal dry-bottom boilers. A number of characterization constants are used to predict ash properties. The most often used are base to acid ratio, silica ratio and dolomite ratio (Table 6). Equations using these constants are usually very sensitive to changes in the amount of alkalis in the ash.

Not all boilers are the pulverized-coal dry-bottom type and in some cases higher than normal CaO in the ash is an advantage. A high CaO concentration in the ash causes a lot of the sulphur to be trapped in the ash as $CaSO_4$ which reduces the amount of SO_2 entering the scrubbers. A high CaO ash may be an advantage in "integrated coal gasification combined cycle" plants (ICGCC) where coal is burned under pressure. A pilot facility in Japan uses a pressure of 2735 kilopascals. In this situation ash must be collected and removed as a fluid and a fluxing ash chemistry is required. Cement plants are not concerned about ash chemistry to the same extent as large power plants and an ash higher in CaO may actually be an advantage. Fluidized-bed boilers burn coal over a bed of granular limestone The coal and limestone particles are fluidized by passing air upward through the bed. The coal burns in association with the limestone and most of the SO_2 released is converted to gypsum. In this type of boiler any additional calcite introduced with the coal is of no consequence. The high CaO content may be an advantage for PCI use. The injection of a fluxing rather than a refractory ash into the bottom of the blast furnace may be preferred.

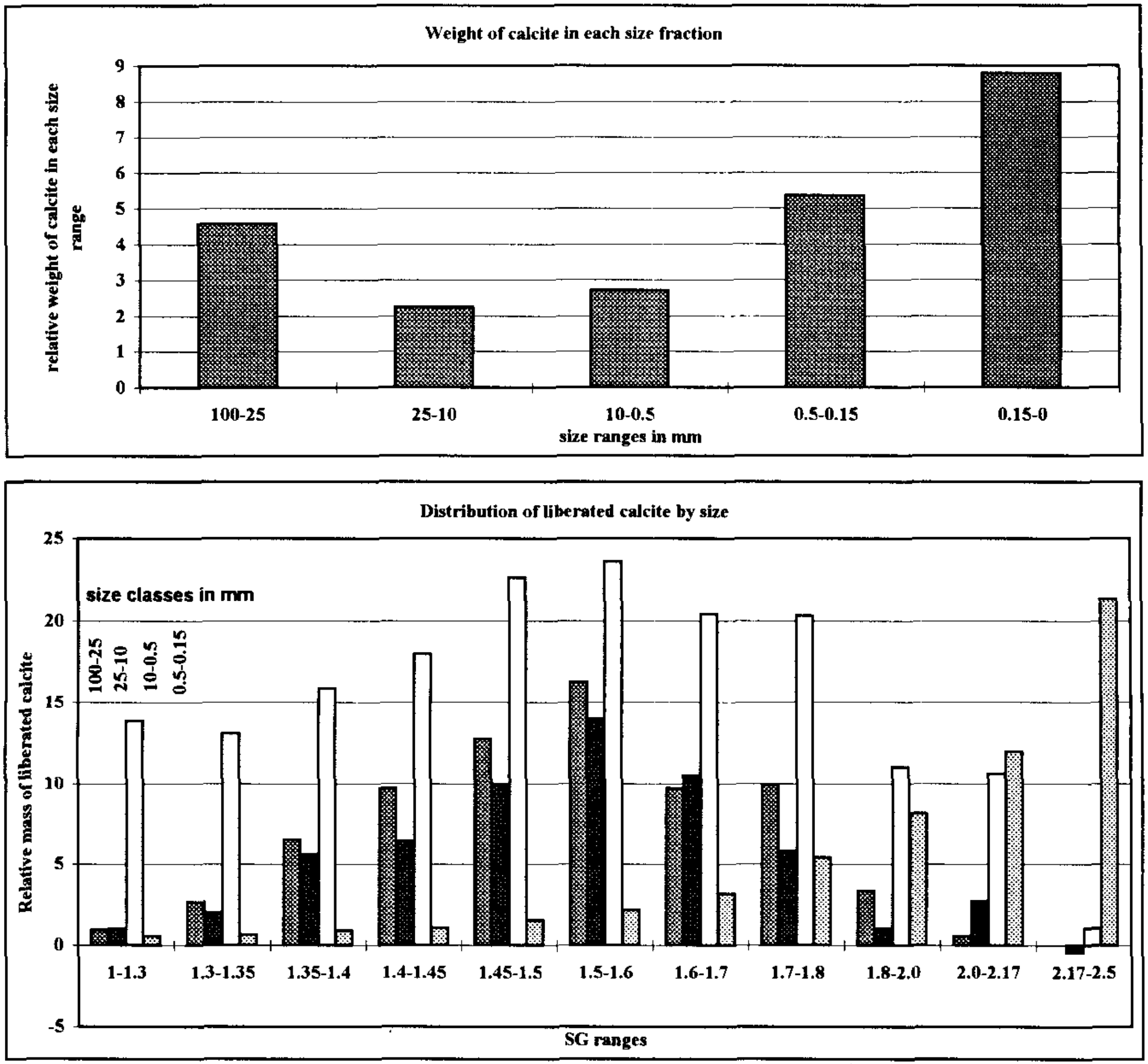

Figure 13. Calcite distributions in single bulk washability data.

Generally CaO, MgO and Fe_2O_3 act as mild fluxing agents in the ash, especially in the presence of excess SiO_2, whereas NaO and FeO act as strong fluxing agents. High and variable CaO in the ash effects a number of slagging and fouling parameters of the ash.

Dry-bottom boilers are not designed to handle much slag and it is important to be able to predict operating conditions that will not produce slag. Historically ash-fusion temperatures have been used as an indication of the slagging potential of the ash. Generally, temperatures measured under reducing conditions are used because they are lower than temperatures measured under oxidizing conditions and there are times when boilers operate at close to reducing conditions. Less emphasis is placed on ash-fusion temperatures today because it has been found that they are unreliable and are not easily correlated with other measures of slagging propensity.

Ash that melts completely over a small temperature range may coat the boiler walls with slag that is difficult to remove. A wider melting range will cause the deposit to solidify on the boiler walls and build up a thicker deposit that may be easier to remove with soot-blowers. The temperature difference between initial deformation and hemispherical deformation is a good measure of the melting range. The temperature range is in part related to the total CaO content. As the CaO content increases the temperature range decreases, and at high concentrations of CaO, the range is reduced, but is insensitive to additional increase in CaO concentration. The point at which the temperature range becomes insensitive to an increase in CaO is about 15%. If the CaO is in this range then increases may not make slagging problems much worse, but blending with a low CaO coal will produce major improvements in slagging properties.

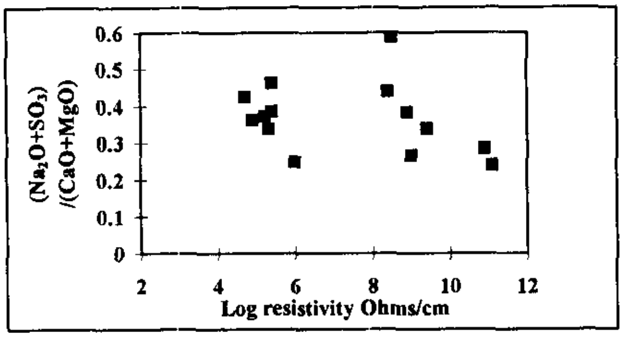

Figure 14. Relationsip of Selle *et al.* (1975) for ash chemistry *versus* ash resistivity using data from Tait *et al.* (1989).

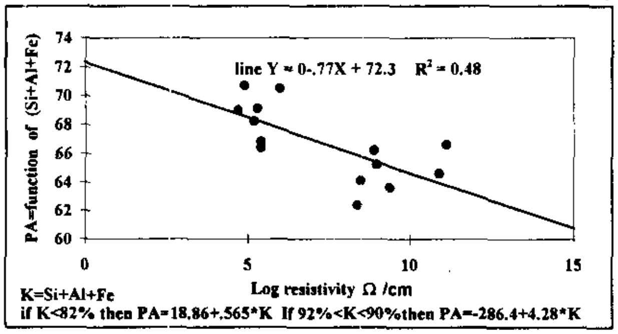

Figure 15. *A plot of electrostatic precipitator efficiency as* predicted by the relationship of Potter (1988) versus actual ash resistivity data from Tait *et al.* (1989).

The temperature at which the ash starts to melt is an important indication of its slagging propensity. Most boilers operate at temperatures in the range 700°C to 1400°C in the combustion area and therefore a non-slagging ash should melt at temperatures above 1400°C. There are number of empirical equations for predicting ash-melting temperatures (Table 6). The temperature at *which slag tends to act as a liquid rather than a plastic* solid is called the temperature of critical viscosity (Tcv) and the temperature at which it has a viscosity of 250 poise (liquid enough to be removed easily as a melt) is referred to as T250°C. Because the equations are empirical, there are often different versions in different references, with confusion as to the correct constants and units.

The equation used to predict Tcv values (Hoy *et al.*, 1965; Table 6) is probably only good to indicate relative trends and not too much emphasis should be put on absolute values. Vorres *et al.* (1986) studied the melting characteristics of synthetic ashes. Their data can be used to compare calculated Tcv temperatures with actual temperature break points in viscosity *versus* temperature plots. The predicted Tcv temperatures are generally within 100°C and higher than the expected value. Attempts by Vorres *et al. to use the Watt and Fereday* (1969) T250°C relationship (Table 6) to duplicate their experimental results were not successful and the equation consistently predicted T250°C temperatures that were too low. They also plotted the predicted temperature *versus* viscosity relationship derived by Hoy *et al.* (1965) with better results. In this study the Hoy *et al.* and Watt and Fereday equations for predicting T250°C provided similar results and the Watt and Fereday equation is used (Table 6).

The adhesion force is a measure of the tendency of the dry or semimolten ash to stick to the boiler walls. Idemitsu Kosan Co ltd. (1993) has published a relationship for adhesive force to silica ratio (Table 6). Idemitsu considers adhesion force to be one of the more useful ash parameters and it points out that it does not necessarily correlate with other factors such as ash-fusion *temperature. It suggests that a value less than 100,* preferably about 10, is required for a coal blend that will not produce fouling in the boiler. Work described by Raask (1985, p. 177) uses the amount of insoluble FeO in the slag to estimate an adhesion index (Table 6). When the FeO in the ash exceeds its solubility limit, the remainder is available to form a strong bond to the boiler walls.

Some alkali oxides form oxide metal compounds and effectively remove metal from the boiler walls. Calcium is a very effective anticorrosive agent when concentrations are above 8% (Skorupska, 1993). The abrasion effect of the minerals in fly ash is dependent on the amount of free quartz and pyrite in the coal.

For efficient operation, electrostatic precipitators require an ash resistivity in the range 10^7 to 10^{10} ohms per centimetre (Tait *et al.* 1989). If the resistivity of the ash particles is too low, they will not hold a charge and will not be attracted to the plates in the precipitator. If the resistivity is too high, the particles tend to insulate the plates and build up a back corona discharge. Generally the collection efficiency increases with increasing ash resistivity within the above range. Fly-ash resistivity decreases as the concentration of metal alkalis increases in the ash (Bickelhaupt, 1975). The presence of Fe_2O_3, K_2O and Na_2O reduces the ash resistivity; CaO, MgO, Al_2O_3 and SiO_2 increase ash resistivity. Some *minerals survive the boiler temperatures and remain in* the fly ash. Clays, if they retain OH, will have low resistivity. The resistivity increases if water is lost, but may remain low if the surviving mineral fragments contain iron. Quartz, on the other hand, has a high resistivity, in the order of 10^{12} ohms per centimetre.

SLAGGING ADHESION AND RESISTIVITY PROPERTIES OF QUINSAM ASH

Slag temperature, adhesion force and fly-ash resistivity are some of the more important ash characterization parameters for thermal coal. The effect of higher than normal and variable amounts of CaO on these and other parameters was investigated using the relationships in Table 6.

Data from Matheson *et al.* (1994) indicate that Quinsam coal has a moderate to low slagging propensity based on a relationship for the lignite-type ash (Table 6):

Slagging factor ≡ (hemispherical temperature + 4 x *initial deformation temperature*)/(5)

TABLE 6
SLAGGING AND FOULING RELATIONSHIPS

ASH CHARACTERIZATION
Base Acid Ratio = $(Fe_2O_3+CaO+MgO+Na_2O+K_2O)/(SiO_2+Al_2O_3+TiO_2)$
Silica Ratio = $SiO_2/(SiO_2+Fe_2O_3+CaO+MgO)$ Dolomite Ratio = $(CaO+Mg))/(Fe_2O_3+CaO+MgO+Na_2O+K_2O)$
Ash type = Bituminous $Fe_2O_3>(CaO+MgO)$ Lignite $Fe_2O_3<(CaO+MgO)$

TEMPERATURE VERSUS VISCOSITY RELATIONSHIPS
$T250°C = 10^7 x M/(\log_{10}(viscosity)-C)^{0.5} + 150$,
$C=.0415 \times SiO_2 +.0192 \times Al_2O_3 +.0276 \times Fe_2O_3 + .0016\ CaO - 4.92$ $M=0.00835 \times SiO_2 + 0.00601 \times Al_2O_3 - 0.109$
Viscosity in poise (Newtons/sec/m^2 =poise x 0.1) Relationship from Watt and Fereday (1969)

$Log_{10}(viscosity)=4.468\ (Silica\ ratio/100) + 1.265(10^4/T_k)-8.44$
Viscosity in Newtons/sec/m^2 T_k Temperature in °Kelvin. Relationship from Hoy *et al.* (1965)

CRITICAL TEMPERATURE
$Tcv = 2990 - 1470 \times A +360 \times A^2 - 14.7 \times B + 0.15 \times B^2$
$A = SiO_2/Al_2O_3$ $B = Fe_2O_3 + CaO + MgO$ Relationship from Hoy *et al.* (1965)

SLAG ADHESION
Slag adhesive force =23.15 - .28 x silica ratio Relationship derived from Idemitsu (1993)

Slag adhesion index $I_{ad}=FeO_{sol} - FeO_{pres}$
$FeO_{sol}=1.2(SiO_2-Al_2O_3)-0.6(CaO+MgO+Na_2O+K_2O+TiO_2)$ Relationship from Raask (1985)

ASH RESISTIVITY
$Log_{10}(resistivity) = D/(0.1632 \times D - 0.00933)$ $D=(Na_2O+SO_3)/(CaO+MgO)$ Resistivity in ohms/metre
Relationship derived from data from Selle *et al.* (1972) for sub-bituminous coals in western USA

if $\sigma<82\%$ then $\sigma_m=18.86+0.565\sigma$ $82\%<\sigma<90\%$ then $\sigma_m=-286.4+4.28\sigma$
where σ = Si+Al+Fe relationship from Potter (1988)
σ_m=collecting area in mass units for a precipitator outlet concentration of 0.1 gm/m^3

ash resistivity log(ohms/cm) = (CaO+1.19)/.859 relationship derived from data in CANMET publication 89-4E

ash resistivity log(ohms/cm) = .7296 x A - 7.48 (R^2=.77)
where $A=-9.474 + .4249 \times SiO_2 + 1.442 \times CaO - .1758 \times K_2O - .6026 \times SO_3$
relationship derived by stepwise multiple regression of all oxides in ash analysis data from CANMET publication 89-4E

or using the relationship for a bituminous-type ash
Slagging factor ≡ (base acid ratio x sulphur)
A plot of ash-fusion temperatures *versus* various oxide contents indicates a weak positive correlation of ash-fusion temperatures with CaO content and base acid ratio and a weak negative correlation with SiO_2, Fe_2O_3 and MgO. The ash-fusion temperatures range from a low of 1265°C to a high of 1410°C (initial deformation temperatures), yet over this range there is no obvious correlation of temperatures with variation in the content of any of the major oxides. A study by Rimmer and Davis (1990) found a negative correlation of ash-fusion temperatures with Fe_2O_3 and a positive correlation with SiO_2, Al_2O_3, TiO_2, MgO and K_2O. Calcium oxide is not mentioned and in fact they state that calcite has little effect on ash-fusion temperatures.

Four Quinsam coal ash chemistries were used to check the effects of CaO on various ash properties. The first is an average of 14 analyses by Matheson *et al.* (1994) and the other three represent modified ash chemistries based on fixing the CaO content of the averaged analysis at 10%, 15%, 20% and 25%, while keeping all other oxides in their correct relative proportions (Table 7).

The results are presented in Table 8. In all cases the ash is defined as a lignite type, based on the definition in Table 6, with a moderate base acid ratio. The silica ratios are generally low, which leads to the prediction of high adhesive forces for the ash.

The predicted Tcv temperatures are generally high and vary from 1549°C at 25% CaO to 1625°C at 10% CaO. The predicted T250°C temperatures appear to be more reasonable and vary from 1135 to 1260°C. Based on the predicted T250°C temperatures, Quinsam coal has a medium slagging propensity (temperature range 1400-1150°C, Tait *et al.*, 1989). The adhesion force and adhesion index of the various Quinsam chemistries are all high (Table 8) because of the low silica index and apparently low solubility of FeO in the ash. All the ash chemistries indicate the potential for fouling in the boiler.

TABLE 7. AVERAGE QUINSAM ASH CHEMISTRY, MODIFIED CHEMISTRIES AND SOME POTENTIAL BLENDS

Sample	SiO_2	Al_2O_3	TiO_2	F_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	S%
Quin av	27.3	27.8	1.93	8.45	22.2	0.6	0.3	0.03	1.4	9.3	0.6
25CaO	26.3	26.8	1.9	8.1	25	0.6	0.3	0.03	1.3	9.0	0.86
20CaO	28.1	28.6	2.0	8.7	20	0.6	0.3	0.03	1.4	9.6	0.68
15CaO	29.8	30.4	2.1	9.2	15	0.7	0.3	0.04	1.5	10.2	0.68
10CaO	31.6	32.2	2.2	9.8	10	0.7	0.4	0.04	1.6	10.8	0.68
LCR	59.1	29.3	2	3	1.4	.3	.1	.5	1.2	.4	.6
BCC	48.2	33.5	2.2	2.5	5.7	1.2	1	.5	1	3.6	.5
FRC	58.4	27.6	1.6	4.7	1.8	.6	.1	1.2	1.1	1.1	.44
TELK	56.8	21.9	1.6	6.14	5.37	1.24	.61	.31	1.25	3	1

Quin av = average chemistry raw data from Matheson *et al.* (1994)
25CaO to 10CaO average chemistries adjusted for 25 to 10% CaO

LCR = Average chemistry Line Creek mine
BCC = Average chemistry Byron Creek Collieries
FRC = Average chemistry of some blends Fording River Collieries
TELK = Average chemistry upper seams
Data from Price and Gransden (1987)

TABLE 8. BLENDS OF QUINSAM COAL WITH OTHER B.C. COALS; EFFECTS ON VARIOUS SLAGGING AND FOULING PARAMETERS

QUINSAM COAL blended with other B.C. coals in 1 to 1 proportions									
Sample	Ash T	Ash	B/A ratio	Dol ratio	Si ratio	AD force	T250	TCV	Ash res
QAV+0	LIG	12	0.59	74.09	44.86	38215	1100	1552	H
Q25%+0	LIG	12	0.62	75.23	43.83	51046	1088	1549	H
Q20%+0	LIG	12	0.5	69.52	48.95	12119	1145	1567	1.70E+11
Q20%+LCR	LIG	12	0.23	63.84	71.95	19	1370	1363	1.90E+08
Q20%+BCC	LIG	12	0.28	67.85	66.35	92	1307	1473	1.40E+08
Q20%+FRC	LIG	12	0.26	60.48	70.38	30	1358	1343	1.50E+08
Q20%+T	LIG	12	0.31	62.84	66.88	79	1330	1272	2.90E+09
Q15%+0	LIG	12	0.41	62.2	54.48	2570	1202	1593	1.70E+06
Q15%+LCR	LIG	12	0.2	56.97	75.02	8	1398	1397	6.20E+06
Q15%+BCC	LIG	12	0.25	62.53	69.46	38	1334	1503	4.40E+05
Q15%+FRC	LIG	12	0.22	53.81	73.38	13	1386	1371	4.90E+05
Q15%+T	LIG	12	0.27	57.34	69.7	36	1356	1293	9.10E+06
Q10%+0	LIG	12	0.32	51.1	60.65	454	1260	1625	L
Q10%+LCR	LIG	12	0.17	47.26	78.26	3	1427	1427	L
Q10%+BCC	LIG	12	0.21	55.28	72.74	15	1363	1529	L
Q10%+FRC	LIG	12	0.19	44.65	76.53	5	1415	1401	L
Q10%+T	LIG	12	0.24	50.01	72.67	16	1386	1325	L
QUINSAM COAL AT 15%CaO blended with Telkwa coal in varying proportions									
15Q1.0	LIG	12	0.41	62.2	54.48	2570	1202	1593	1.70E+06
Q.9+T.1	LIG	12	0.38	61.42	57.84	999	1233	1517	2.40E+06
Q.8+T.2	LIG	12	0.35	60.55	61.04	408	1264	1443	3.30E+06
Q.7+T.3	LIG	12	0.32	59.59	64.07	174	1295	1387	4.70E+06
Q.6+T.4	LIG	12	0.30	58.53	66.95	77	1326	1335	6.50E+06

Q	Quinsam
LCR	Line Creek Resources
BCC	Byron Creek Collieries
FRC	Fording River Coal
T	Telkwa

% numbers indicate % of CaO in Ash
.7 indicates mixing proportions
All samples assumed to be 12 % ash
Equation used for predicting relative ash resistivities
not applicable outside a range of 1E+5 TO 1E+12

Ash T	LIG or BIT for lignite or bituminous
B/A	base acid ratio
Dol	dolomite ratio
Si	silica ratio
AD	adhesion force
T250	temperature at 250 poise
Tcv	critical viscosty temperature
Ash Res	ash resistivity in Ω /cm H value above 1E+12 L value below 1E+5

The high CaO content of Quinsam coal will ensure that it will not cause corrosion. No estimates of erosion are made in Table 8, but because Quinsam ash appears to be low in free quartz and it is not expected to cause excessive ware of the pulverizers or erosion in the boiler. Pyrite can also cause erosion, but the raw samples analyzed in this study averaged about 0.68% total sulphur of which about 0.13% is probably pyrite. Consequently there will be very little pyrite in the washed coal available to cause problems.

Based on its high CaO content, Quinsam coal will have a high ash resistivity. The relationship suggested for sub-bituminous coals by Selle *et al.* (1972; Table 6) indicates that ash resistivity increases as the concentration of CaO increases. This relationship was tested using data from Tait *et al.* (1989; Figure 14) and does not appear to be useful for a broad range of Canadian coals. Potter (1988) uses the sum of Si, Al and Fe to predict electrostatic precipitator performance in terms of surface area required to collect a fixed amount of ash. This relationship was also tested and a weak inverse correlation of plate area to ash resistivity is apparent (Figure 15).

A correlation analysis of all the oxides in the ash *versus* ash resistivity, in Tait *et al.*, indicates that the best correlation with a single oxide is for CaO (Figure 16). The relationship is only approximate and is only substantiated over a range of CaO content from 4% to 15%. The R-squared value for the best-fit line is 0.7. A stepwise multiple regression analysis of the same data provided the best fit of the actual resistivity data to a function of ash chemistry (Figure 17, $R^2 = 0.77$). The analysis indicates that CaO, SiO_2, K_2O and SO_3 are the important oxides influencing ash resistivity. The data set from Tait *et al.* (1989) includes samples from the Elkview and Greenhills mines in southeast British Columbia. Measured ash resistivities for samples from these two mines were 7.9 x 10^4 and 2.0 x 10^5 ohms per centimetre, respectively, and these values can be compared to industrial results on the same well known coals to indicate whether the predicted resistivities should to be adjusted up or down. The present multiple regression equation which predicts resistivities over a range of 10^5 to 10^{12} ohms per centimetre is used to predict the resistivities for the Quinsam coals. If the predicted resistivity is outside these limits then it is designated simply as high or low in Table 8 because it is unlikely that there is a linear relationship outside the range of the data. The resistivities of Quinsam coal are high when the CaO content is above 20%. They are in the required range for CaO contents from 20% to 15% and are low for CaO contents of less than 10%.

SLAGGING AND FOULING CHARACTERISTICS OF BLENDS OF BC THERMAL COALS

Most power plants burn a blend of pulverized coals so it is useful to investigate the effect on slagging and fouling parameters of blends of coals containing Quinsam coal. Because most slagging and fouling parameters have non-linear relationships to ash chemistry, it is often not apparent what the characteristics of a blend will be until the calculations are made. A computer program was used to calculate the blended ash chemistry of any number of coals, based on blend proportions and the amount of ash in each coal. The program then calculates the slagging and fouling parameters defined in Table 6.

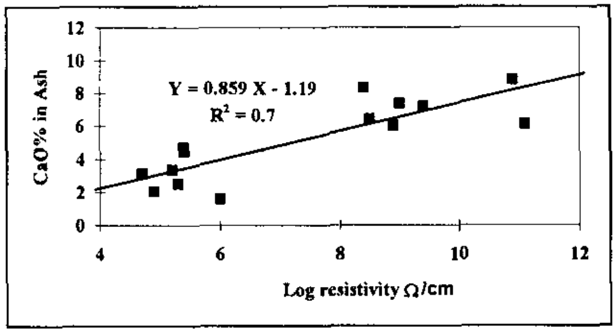

Figure 16. A plot of CaO% in ash *versus* actual ash resistivity data from Taite *et al.* (1989).

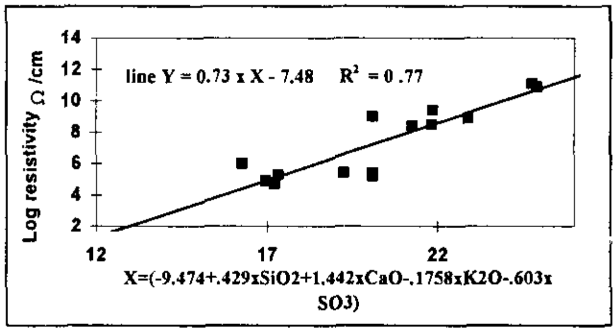

Figure 17. Plot of the results of multiple stepwise correlation analysis of ash oxide data and actual ash resistivity data, from Tait *et al.* (1989).

A number of theoretical blends of ash oxide chemistry were created which mixed other British Columbia coals with varying proportions of Quinsam coal. The resulting ash chemistries are listed in Table 7 and the predicted slagging and fouling parameters are in Table 8. All coals were assumed to have 12% ash which is in the mid-range for acceptable thermal coals. The Quinsam coal was blended with average analyses reported in Price and Gransden (1987) for the lower seams in the Mist Mountain Formation at Line Creek mine (LCR), for upper Mist Mountain Formation seams from the Fording River Coal mine (FRC) and the basal Mist Mountain seam from the Byron Creek Collieries (BCC). An average analysis was also obtained for coal from the Telkwa exploration property which is a potential thermal coal mine. All the blends have lignite-type ash chemistry as defined in Table 6. All the slagging parameters based on T250°C values are improved when Quinsam coal is blended with coal from southeast British Columbia, except for Byron Creek coal which also tends to have moderate amounts of CaO in the ash. Most of the blends have low slagging propensity (T250°C > 1275°C) and some have T250°C values close to 1400°C, indicating no slagging propensity.

The adhesion force of the ash is greatly reduced in all cases and the 15% CaO Quinsam coal blends achieve adhesion forces close to the value of 10, which is considered to be an acceptably low value for minimal slagging problems.

Based on the relationship of CaO% to ash resistivity derived from the combustion data in Tait *et al.* (1989), ash resistivities of blends of Quinsam coal with other British Columbia coals decrease and are acceptable for most blends.

CONCLUSIONS

Some Upper Cretaceous coals on Vancouver Island have higher CaO contents than most high-volatile bituminous coals. Preliminary data indicate that seams higher in the coal-bearing sections may have more normal CaO contents.

The Quinsam mine is presently mining the lowest seam in the coal section in the Comox Formation and this seam has higher than normal CaO contents. The CaO originates in the coal as calcite which is on cleat surfaces and also may be dispersed in the coal. Because the calcite is associated with the coal and not the rock partings, washing the coal to remove the ash may result in higher concentrations of calcite in the wash ash. There is less than 1% CaO in the ash originating from minerals other than carbonates and there is from 0.0% to 7.5% CaO dispersed as calcite in the coal.

Because most of the CaO in the sample is present as calcite, a simple acid leach and weighing test can provide a moderately accurate way of estimating the total CaO in the sample.

The calcite does not liberate from the coal as easily as might be expected. This may be because some is dispersed through the coal and not coating the cleat surfaces. Crushing the coal to less than 100 millimetres top size produces complete liberation of about 20% of the calcite. Crushing to less than 25 millimetres top size would probably increase the calcite liberation from 20% to 30%. An alternative approach in the plant, which would produce less -0.15-millimetre material would be to screen and recrush only the 100-25-millimetre material. This should produce the same increase in calcite liberation without a large increase in the amount of fines.

The high CaO in the ash has a number of effects on its behaviour in a boiler. The melting temperature is reduced which may increase slagging. The stickiness of the ash, measured by adhesion force, increases and this can increase fouling propensity. The ash resistivity in the electrostatic precipitators increases. If the resistivity is sufficiently high then this may reduce the efficiency of the precipitators. High CaO content may aid in sulphur removal and help to limit metal corrosion in the boiler. The low content of free quartz in Quinsam coal helps reduce erosion in the boiler and wear on the pulverizer.

At Quinsam, the CaO content of the ash can be lowered at the expense of introducing more pyrite and sulphur. In terms of electrostatic precipitator performance this may be advantageous; the addition of iron and sulphur will lower ash resistivity and the extra sulphur is unlikely to overload the scrubbers because the CaO content will remain high and will remove much of the added sulphur as $CaSO_4$ in the bottom-ash deposits.

Blending Quinsam coal with other thermal coals can produce a thermal coal with acceptable ash properties, including slagging propensity, adhesion and ash resistivity.

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