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THE UNIVERSITY OF British Columbia

MINERAL MATTER CONTENT AND GROSS PROPERTIES

OF HAT CREEK COAL

DEPARTMENT OF METALLURGY

VANCOUVER, BRITISH COLUMBIA • CANADA

""Mineral Matter Content and Gross Properties of Hat Creek Coal"

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(B.C. Hydro and Power Authority)

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Introduction

The Hat Creek coal deposit contains a complex array of inorganic minerals including a high proportion of those that can be classified as clay minerals. The use of this coal is highly dependent on knowledge being gained of the quantities and properties of these minerals. The objective of this study is to provide information, which may help in developing methods for beneficiating coal and alternate use of the inorganic minerals (including claystone). To fulfill the above objective, it is proposed that a study be made to identify and quantify the inorganic minerals using x-ray diffraction, thermal analysis and It is further proposed that a study be made of the application of thermal SEM. analysis and gas chromatography to determine the gross properties of the organic component of the Hat Creek coal. Recent development in utilizing the thermal analysis technique (TGA) for proximate analysis of coal i.e. to determine carbon, volatile content, non-combustible and fusion temperature will also be investigated. Application of a Pressure Differential Scanning Calorimeter to determine the heat-content of a coal will also be explored. These studies should serve to establish the pattern of coal analysis that would be essential for the Hat Creek coal development.

Materials

A range of samples of coal was supplied by B.C. Hydro initially. Subsequently, a batch of clay samples (overburden) and one sample of ash were supplied for analysis as described above. The coal samples are designated as 'A' series and identified as follows:

<u>A-Series</u>

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B.C.	Hydro	identification	code
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76-135-91			A1
76-135-93			A2
76-135-135		,	A3
76-135-137	(1195'-1205')		A4
76-135-41	(685'-695')		A5
76-135-43			A6
76-135-120	(905'-910')		A7
76-135-121	(910'-920')		A8
76-135-163			A9
76-135-164			A10

The clay samples are designated as 'B' series and identified as follows: B-Series

B.C.	Hydro identification code		Color code*
	DDH 76-191 X-4 238.6-238	Bl	4
	DDH 76-191 X-5 298.2-298.5	B2	4,1
	DDH 76-191 X-6 388.1-388.4	B3	3 .
	DDH 76-191 X-7 464.7-465.0	В4	5
	DDH 76-181 X-8 537.8-533.1	В5	4
	DDH 76-191 X-9 706.2-706.5	В6	2
	DDH 76-191 X-10 744.7-745.0	в7	3
	DDH 76-191 X-11 809.1-809.5	B8	3,5
	DDH 76-191 X-12 1285.6-1286.0	В9	3,5
	74-24-348-350	B10	5
	76-123-399-402	B11	. 5
	76-135-296-301	B12	4

76-136-219-221		B13	5
V76-345D DDH 76-135	S135-6	B14	3
V76-345D DDH 76-135	S135-X1	B15	4
V76-345D DDH 76-135	S135-2	B16	4
V76-345D DDH 76-191	S19164	B17	3
V76-345D DDH 76-191	S191-71	B18	2
V76-345D DDH 76-191	S191-70	B19	3
(special) 76–144–442		в20	

* color variation

Very dark	<u>dark</u>	medium	<u>light</u>	very light
1	2	3	4	5

Ash Sample

One ash sample supplied by Mr. Max French of B.C. Hydro was undesignated.

Although the clay specimens were sent at an intermediate stage of this investigation, the results on clay samples will be reported first, as this part of the investigation has been completed.

Experimental Procedures

A. Clay Samples (B Series)

The clay samples were found to be quite heterogeneous in nature. Their colour varied from one sample to another and even within one sample there was variation in colour. For this, the samples were ground and mixed thoroughly for homogeization and sampling. The identification of the minerals was carried out by x-ray diffractometric scanning from 3° to 95° of 20 of all samples. Attempts were made to assign all diffractometric peaks obtained on each specimen. Supporting evidence of the diffraction analyses was obtained by Scanning Electron Microscopy. X-2ay diffraction scans were also made on glycolated samples to differentiate between illite and bentonite (montmorillonite).

It should be pointed out that no attempt was made to identify minerals which are present in a very minor concentration i.e. less than 2-3%, which is the detectable limit by the diffraction technique.

Once the minerals present were identified, the estimation of these minerals was done by adding 10% by weight of magnesia and using it as the internal standard. Initially several standard calibration curves were made using synthetic mixtures of known quantities of different minerals identified in the clay samples, again using magnesia as the internal standard. One diffractometric peak of each of the minerals was integrated (integrated photon count) and normalized with respect to the integrated peak intensity of magnesia. The ratio of the integrated peak areas are plotted as a function of the ratio of the quantities, which are known. The standardized calibration plots were subsequently used to calculate quantitatively the amount of different minerals present in a clay sample. Again all integrated peak areas were normalized with respect to the internal standard, before using for estimation of minerals.

The estimation of minerals, as carried out by this technique, can be considered to be accurate to within \pm 3% for felspar, quartz and kaolinite, but only within \pm 5% for bentonite.

The results for the quantitative determination of minerals, as carried out by the x-ray diffraction analyses are shown in Table I (next page). <u>Please</u> <u>note:</u> In addition to the minerals reported in the table the following minerals were also checked, if they are at all present even within a few percent (> 3%).

- 4 -

Table 1	Ta	ble	ĩ
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Sample Number	Quartz	Kaolinite	Bentonite	Siderite	Feldspar	Epidote
DDH 76-191			*****			Zone
X-12-1 1285.6-1286.0	43	54	_	3	_	- Below
X-12-2 1285.6-1286.0	35	65	· _		-	- Below
X-11-1 809.1-809.5	46	46	-		8	- C.
X-11-2 809.1-809.5	45	51	·	4	-	- C
X-10 744.7-745.0	33	67				- B
X-9 706.2-706.5	47	53	trace	-		- Ĝ
*X-8 537.8-533.1	22	29	38		11	- Ä
X-7 464.7-465.0	17	47	36	trace	-	- A
*X-6 388.1-388.4	11	68	15	-	6	- A
X-5-1 298.2-298.5	20	48	19	-	13	- A
X-5-2 298.2-298.5	12	58	30	-	- ·	- A
X-4 238.6-238.9	8	55	22	trace	15	- 6
*74-24-348-350	9	10	71	_	10	- Above
76-123-399-402	11	3	69	13	4	- Above
76-135-296-301	13	47	34		6	- Above
*76-136-219-221	8	11	79	-	2	- Above
76-144-442	49	1.5	29	-	7	-
V76345D DDH 76-135						
S135-6 661.0-661.3	34	52	14	_	trace	- A
S135-X1 557.5-557.7	24	27	39	~ .	10	- 14
\$135-2 534.1-534.5	31	37	26	6	-	- A
V76345 DDH 76-191						
S191-64 645-645.5	19	51	_	19		11 3
S191-71 950.2-950.8	38	62	trace	-	-	- C
S191-70 895.1-895.6	44	56	·	trace		- C

* Glycolated tests performed

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Pyrophyllite, Serpentine, Halloysite, Dolomite, Magnetite, Apatite, Pyrite, Augite, Galena, Sphalerite, Tetrahedrite, Ankerite, Labradorite, Chalcopyrite and Hyalophane.

1+8

To differentiate between bentonite and illite, glycolated tests were performed on clay samples and re-x-rayed for peak-shift.

Sample - 76-144-442

The specimen designated as 76-144-442 is a special sample. It is very light in weight and has a fibrous texture on a fractured surface. X-ray diffraction traces showed that it essentially contains quartz, bentonite and felspar with a small amount of kaolinite but it also gave a medium strong diffraction peak which could not be assigned to any of the above minerals. No attempt has been made to do an exhaustive search for this particular peak but elemental analyses by scanning electron microscopy showed that it contains significant amount of strontium and phosphorous as shown in Figure 1. Significance of the presence of these two elements is not known. This sample was also fractionated by sedimentation into 3 different size fractions: coarse (settled for 5 minutes), medium (settled for 6 hours) and fine (balance remained in suspension). The ratio of these 3 size fractions was found to be 0.59 (for coarse), 0.28 (for medium) and 0.13 (for fine). No significant variation of minerals was observed in different size fractions. The average diameters of the particles in different size fractions are > 20 µm (for coarse), < 20 > 2.5 um(for medium) and < 2.5 µm (for fine). For particle size calculations see appendix 1. Glycolation test was also performed on this sample. If time permits, we would like to do some more analyses on this sample.

 $* 2\theta = 24.1$ d = 3.69 Å

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- 6 -



Before we proceed to consider our studies on coal, we would like to describe our investigation on ash. This ash was supplied as a 2-lb batch by Mr. Max French, which according to the information supplied was produced by burning a batch of Hat Creek coal in Canadian Combustion Research Laboratories, Ottawa. An exhaustive study was made on this ash, with respect to its mineral content, unburnt carbon and elemental analysis. Furthermore, this ash was also fractionated into 2 size fractions by sedimentation; coarse (> 20 µm) and fine (< 20 µm). The results are as follows:

> Coarse (> 20 μm) - 96% (by wt.) Fine (< 20 μm) - 4% (by wt.)

The minerals present were identified by x-ray diffraction, as discussed earlier, but no effort was made to determine them quantitatively. The results are shown in the following table.

Table II

Mineralogical analysis of The Ash Sample

As received	Cristobalite	Mullite	a-Fe ₂ 03	A1-9	Si-Spinel	Quartz
Coarse fraction	**	81	13	•	13	tt
Fine fraction	**	**	11		11	`11

The amount of unburnt carbon was not detectable (< 0.4%). This was determined from the weight lost, when this ash was reburnt for another 10 hours at 800°C in air. From the mineralogical analysis it can be concluded that the temperature this coal was subjected to is over 1000°C and more likely over 1200°C. The transformation of impure quartz to cristobalite can occur above 1000°C,

Ash

but more readily above 1200°C. All clay minerals (kaolinite, bentonite and illite) are transformed to mullite above 1200°C. Existence of a small amount of alumino-silicate spinel indicates that some region of the flame was below 1200°C. When the clay minerals passed through this region, they transformed to Al-Si-spinel rather than mullite, as the transformation sequence can be approximately summarized as follows:

> $\sim 600^{\circ}$ Clay Minerals → Minerals → Al-Si-Spinel \downarrow > 1200°C

> > Mullite

Similarly, retention of a small amount of quartz, the main mineral constituent of sand is indicative that either the temperature of a certain region of the flame (burner) was below 1200°C or some of the sand grains are too large, as the quartz to cristobalite conversion is particle size dependent. Large grains of quartz are kinetically too slow to convert at lower temperatures (below 1470°C).

Elemental Analyses of Ash

For the sake of comprehensiveness of the study, we also performed elemental analyses (qualitative) by the x-ray analyser attached with the scanning electron microscope. Elemental identification was also carried out in order to substantiate the findings of x-ray diffraction analyses. Two x-ray scans of ash are shown in Figures 2 and 3. In addition to elements expected to be present, e.g. Al, Si, Ca, Fe, Mg etc., we encountered both Cu and Ni in significant quantities. However, Cu and Ni is not evenly distributed in all the samples. In the majority of cases, these two elements were not encountered while





searching over the whole specimen (~ 50 milligrams). Occasionally however, we encountered these two elements and on further search, we found the existence of Cu and Ni bearing minerals as shown in Fig. 4(a-d). Minerals of Fe and Cu sulphide are shown in Figs 5 and 6 (a-e); and mineral of Fe, Ni and Cu is shown in Fig. 7 (a-e). This ash was analysed also by Chemex Laboratories Ltd., North Vancouver, they reported the concentration of Ni and Cu below 100 ppm. It is most likely that the background counts of these two elements are below 100 ppm and that is what has been obtained by spectrographic analysis of the ash sample. It is necessary to search for the sulphide minerals before these could be detected. But it is apparent from our SEM analyses that there can be a significant concentration of sulphide minerals of Ni and Cu in the ash sample. And this needs further thorough investigation. It should be pointed out here that the origin and history of the ash is not known. It is possible that the sulphide minerals are contaminant from the pulverizing and grinding operations. But the extent of their occurrences in the ash sample makes this less likely.

Coal Samples

As discussed earlier, ten samples of coal were supplied to study their mineral content, fixed carbon, ash, heat content (calorific value) and moisture. With the suggestion of Mr. Max French, we started with 4 samples A1(91), A2 (93), A3 (135) and A4 (137). These pairs (91-93 and 135-137) are from the same drill cores but at different depths, and also have different fusion temperatures.

The coal samples were separated into coarse, medium and fine fractions by sedimentation. Five grams of coal sample and 750 ml of H_2^0 were used. The material was allowed to settle for 5 minutes, the settled component constituted

- 9 --

Figure 4

Copper and Nickel bearing minerals at 620X









Figure 5

Iron and Copper sulphide mineral

1000x











Figure 6

Iron and Copper sulphide mineral

1000x



Figure 7

Iron, Nickel, and Copper mineral

460X











1000 X



Si 1000 K

Cu

1000X

the coarse fraction. The medium fraction consisted of material settled for 6 hours (after 5 min fraction was removed). The solid fraction left unsettled was considered to be the fine fraction. The average particle diameter for these size fractions is shown as follows:

(Appendix I).

Coarse - > 20 micron (µm) Medium - <20>1.5 (µm) Fine - < 1.5 µm.

X-ray diffractometry provided the means of identifying minerals present in the various size fractions. Actual quantitative analysis was done using MgO as an internal standard, as discussed earlier. Integrated areas under characteristic peaks of the minerals were compared with that of the standards.

Scanning electron microscopy (SEM) was found to be a valuable tool for identifying the minerals present. In spite of the fact that this is a qualitative analysis, it gave an approximate amount of each element present in different samples. Only by knowing the elements present that an accurate identification of minerals is possible.

Thermogravimetric analyses (TGA) gave the amount of clay minerals in each fraction of a coal sample. By knowing the weight of each fraction, the weight of clay material in each fraction and the percentages of the minerals present can be calculated.

The percentages of the minerals present in each coal sample are shown below, and are expressed as percent of the total inorganic materials.

<u>Table III</u>

Inorganic Mineral Content in Coal

Sample	Kaolinite	Quartz	Siderite	Bentonite	Felspar	Epidote
A ₁ (76-135-91)	25	17	12	1	Trace	8
*A ₂ (76-135-93)	33	31	8	Trace	Trace	~ _

Also a trace amount of pyrite is present in this sample.

The mineral distributions in different size fractions are shown in Table IV. Unfortunately however, at this stage of the investigation, the thermogravimetric unit was broken down. The spare parts needed for replacement has arrived during the first week of January, 1977. (2 months after sending the order). Two plots on TGA for sample number A_1 and A_2 are shown in Figures 8 & 9. This equipment appears to provide a large amount of informations on coal. As a matter of fact, the whole proximate analysis can be done in a single run, which takes only 45 minutes. As shown in the plot the three consecutive weight losses can be attributed to moisture (adsorbed), volatile matter (including dehydroxylation of clay minerals) and fixed carbon. Any weight loss resulting from the decomposition reaction e.g. FeCO₃ \rightarrow FeO + CO₂, during the combustion of coal should be taken into consideration while calculating fixed carbon content. The non-combustible product remaining above 750°C is primarily ash which is also obtainable from the plot. The data calculated from these curves are shown in Table V.

Table IV

Inorganics of Coal Samples

(5 g. of each was used for fractionation)

Sample Number		Kaolinite	Quartz	Bentonite	Siderite	Epidote	Feldspar	Pyrite	Total Weight	Percentage of 5 g. sample	
76-135-91	Coarse Medium* Fine*	36% 51% 65%	27% 29% 25%	- 9% 10%	22% -	15% - -	11%		4.64g 0.10g 0.26g	93% 2% 5%	1.000
76-135-93	Coarse Medium* Fine*	42% 48% 69%	45% 39% 28%	- 3%	13% 		5%	3%	4.38g 0.18g 0.45g	87% 4% 9%	dien 1
76-135-135	Coarse Medium Fine	33% 41% 62%	36% 45% 37%		22% 12% 1%	9% 2% -		- trace -	3.75g 0.89g 0.36g	75% 18% 7%	6043
76-135-137 1195'& 1205'	Coarse Medium Fine	44% 62% 60%	43% 38% 40%	- - trace	7% trace	3%	3%	- trace -	3.46g 1.08g 0.46g	69% 22% 9%	-ie:

Coarse fraction: settled for 5 minute

Fine fraction: the rest Medium fraction: settled for 6 hours after . coarse fraction was removed.

*Medium fraction: settled overnight after

*Fine fraction: the rest

coarse fraction was removed.

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TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES



TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

<u>Table V</u>

	Moisture %	Volatile (dehydroxylation) %	Fixed Carbon* (Uncorrected) %	Ash Content %
A ₂	8.6	17.1	17.7	56.6
Dolmage Campbell analysis	18.58	28.43	14.90	56.67
A1	4.6	20.0	22.0	53.2
Dolmage-Campbell	20.50	22.31	15.46	62.23

Proximate Analysis of Coal by TGA

* The weight loss due to siderite decomposition (FeCO₃ → FeO + CO₂) is ~ 38% by weight. If this correction is applied, then the fixed carbon for A₂ becomes 14.66 wt%, in agreement with the value reported by Dolmage Campbell. For A₁ sample, the fixed carbon value will reduce from 22.0 wt% to 17.5 wt%. However, the samples used for this analysis by TGA were dried at 80°C prior to the experiments which reduced part of the moisture from the sample supplied. Part of the discrepancies can be accounted for this error. Further work will be conducted as soon as the TGA equipment becomes operational.

The results of the elemental analysis as carried out by SEM are shown in Table VI, conforming to the findings of X-ray analysis, except in some samples, both Cu and Ni are detected. This work is continuing with all the other six samples sent for investigation. In addition, the pressure differential scanning calorimetry cell has just arrived. This will be used to study the heat content (calorific value) of all coal samples and compared with the values determined by Dolmage Campbell Associates by the conventional technique.

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Summary of SEM findings

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	76-135-91	75-135-93	76-135-135	76-135-137	76-135-41	76-135-43	76-136-120	76-136-121	76-135-163	76-135-164
Aluminum	1	√	√	/	1	1	√	1	1	/
Silicon	1	\checkmark	✓ .	\checkmark	1	1	\checkmark	\checkmark	- √	1
Calcium	\checkmark	\checkmark	\checkmark	\checkmark	1	1	\checkmark	\checkmark	\checkmark	\checkmark
Potassium	· 🗸	✓ .	\checkmark	\checkmark	\checkmark	1	V	V	\checkmark	\checkmark
Titanium	1	\checkmark	\checkmark	\checkmark	\checkmark .	\checkmark	. √	\checkmark	\checkmark	\checkmark
Iron	· 1	✓ .	\checkmark	\checkmark	\checkmark	1	\checkmark	\checkmark	· 🗸	\checkmark
Magnesium	-	?	?	~	-	-		-	· _	
Sulphur	1	\checkmark	1	1	1	1	1	\checkmark	√ √	√
Lead	1	- /	\checkmark	\checkmark	\checkmark	?	1	√	\checkmark	· 🗸
Molydenum*	/ **	?	\/**	?	12:32	**	**	**	·/**	/ **
Zinc	~	-		_	-	-			-	-
Sr	?	?	?	· 🛏	-		?	?	-	?
Nickel	-	-	-	?	-	-	-	-	-	-
Copper	-	-	-	_	-	-	-	-	·	, 🗕
Bromine	-	-	-	-	-	-	-	-	-	-
Mn	-	· _	\checkmark	· -	-		~~	-	-	-
Na		. –		√		-	-			

* Mo uncertain because of noise effects

** ${\rm K}_\beta$ (of Mo) peaks present

? uncertain if element is present

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APPENDIX I

Sedimentation Analysis

Stokes' Law:

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$$V = \frac{2(p_1 - p_2) gr^2}{9 \eta}$$

V is the velocity of fall in cm per second.

n is the viscosity of liquid (water at $20^{\circ}C = 0.01$ poise.

 $p_1 & p_2$ are respectively the density of the particles and the

liquid medium.

g is gravity (981 cm/sec²)

r is the radius of particles in cm.

$$V = \frac{S}{t} \qquad S \text{ Height t: time} \quad .' \cdot \frac{S}{t} = \frac{2(p_1 - p_2)gr^2}{9n}$$

,', r = $(\frac{9nS}{2t(p_1 - p_2)g})^{\frac{1}{2}}$

specific gravity of kaolinite = 2.61

Assume average specific gravity $\simeq 2.6$ or density $\simeq 2.6 \frac{g}{cm^3}$

$$S \approx 13 \text{ cm}$$

 $p_1 \approx 2.6 \text{ g/cm}^3$
 $p_2 \approx 1.0 \text{ g/cm}^3$

5 minutes 300 sec =

$$r = \left(\frac{9(0.01 \frac{g}{\text{cm sec.}})(13 \text{ cm})}{2(300 \text{ sec})(2.6 - 1.0 \frac{g}{\text{cm}}) 981 \frac{\text{cm}}{\text{sec}^2}}\right)^{\frac{1}{2}}$$

= $(1.24 \times 10^{-6} \text{ cm}^2)^{\frac{1}{2}}$
= $1.1 \times 10^{-3} \text{ cm}.$

Coarse fraction consists of particles with radius of about 0.001 cm. Diameter of these particles is 0.002 cm (assuming spherical particles). 6 hours = 21600 sec. t

$$r = \left(\frac{9(0.01 \frac{g}{cm \ sec.}) (13 \ cm)}{2(21600 \ sec) (2.6 - 1.0 \ \frac{g}{cm^3}) (981 \ \frac{cm}{sec^2})}\right)^{\frac{1}{2}}$$

= $(1.73 \ x \ 10^{-8} \ cm^2)^{\frac{1}{2}}$
= $1.3 \ x \ 10^{-4} \ cm$

Medium fraction consists of particles with radius of about 1.3 x 10^{-4} cm or diameter of 2.6 x 10^{-4} cm (assuming spherical particles)

Fine Fraction

2

Ref. Colloidal Chemistry by R. J. Hartman QD 549 H19 1947, p. 171 + 173. The radius of the clay particles could be calculated using the centrifugalization equation. The angular velocity of the centrifuse used was measured using a techameter.

$$r = \left(\frac{9\eta \ln(x_{1}/x_{0})}{2 dw^{2}(t_{1}-t_{0})}\right)^{\frac{1}{2}}$$

: viscosity of liquid = 0.009 poise at 25°C η

: speed of rotation = 3014 rpm \approx 50.2 rps $\approx 2\pi r_1$ (50.2 rps)(r₁=10.4 cm) w $\approx 3.28 \times 10^3$ cm/sec.

d : absolute density (2.6 g/cm³ average value of sample) x : distance measured from the center of rotation. The position of the particles is x_0 at time t_0 , and x_1 at time t_1 .

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$$r = \left(\frac{9(0.009 \ \frac{g}{\text{cm sec}}) \ln (12.1/10.4)}{2(2.6 \ \frac{g}{\text{cm}^{3}}) (3.28 \ \text{x} \ 10^{3} \ \frac{\text{cm}}{\text{sec}})^{2} (1.2 \ \text{x} \ 10^{3} \ \text{sec.})}\right)^{\frac{1}{2}}$$

= $(1.83 \ \text{x} \ 10^{-13} \ \text{cm}^{2})^{\frac{1}{2}}$
= $4.3 \ \text{x} \ 10^{-7} \ \text{cm} \ \Rightarrow \ \text{diameter of particles} \simeq 8 \ \text{x} \ 10^{-7} \ \text{cm}.$

Therefore the range of range of particle size in the fine fraction is $\approx 2.6 \times 10^{-4}$ cm to 8×10^{-7} cm.