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APPROBATIONS

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The Effect of Bitumen Adsorption on the Sedimentation Behaviour of Coarse Bi-Wetted Solids Separated From Syncrude Sludge Pond Tailings

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For: Sludgementals Consortium c/o AOSTRA

Key Words: Bi-wetted solids, Sludge Flocculation, Structure

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EXECUTIVE SUMMARY

OBJECTIVE

To determine the role of coarse bi-wetted solids in sludge structure.

ACHIEVEMENT

- Bi-wetted (BWS) solids were separated from Syncrude sludge pond tailings.
- Bi-wetted solids were characterized by Energy Dispersive X-ray analysis (EDXA), Scanning Electron Microscopy and Leco carbon and sulphur analysis.
- Flocculation characteristics of BWS were determined using oil phase agglomeration techniques.
- Flocculation behaviour of a sample of Sub-bituminous coal was also investigated for comparison purposes.

TECHNIQUE DEVELOPMENT

- A fractionation scheme for the separation of BWS was developed.
- A test was developed to investigate the flocculation behaviour of BWS.

HIGHLIGHTS

- Bi-wetted solids have similar surface characteristics to sub-bituminous coals which are known to exhibit flocculation behaviour in the presence of immiscible liquids of different polarity.
- Bi-wetted solids are associated with a high iron content. In other work iron analysis has been used as one indicator for sludge production potential. It is possible therefore that the BWS, with their high iron content play a role in sludge formation.
- The results of this investigation were inconclusive because of the presence of varying amounts of more hydrophobic solids as contaminants in the BWS samples separated. However, in some of the trials conducted a significant increase in sediment volume was noted after treatment.
- The implication of these results is that the BWS solids could be involved in sludge formation, either as a primary or secondary structure.

RECOMMENDATIONS AND FUTURE WORK

Future work will concentrate on refining the separation technique to produce a more uniform material (from a surface wettability point of view). The flocculation behaviour of this material alone and in the presence of ultrafine gel formers will be determined.

ABSTRACT

A fractionation scheme has been developed to separate the so-called bi-wetted solids, (BWS) from Syncrude sludge pond tailings. Several samples of BWS were prepared using this scheme. These solids have similar surface characteristics to sub-bituminous coals which are known to exhibit flocculation behaviour in the presence of immiscible liquids of different polarity. In this work oil phase agglomeration techniques were used to investigate the behaviour of the BWS solids, suspended in water, in the presence of minor amounts of bitumen solution in Stoddard solvent (60 w/w%), in an attempt to determine their flocculation characteristics. These tests were carried out by following the gravity settling of slurries produced after agitating samples of BWS with bitumen solution in pond water. These solids are associated with a high iron content.[1] In other work iron analysis has been used as one indicator for sludge production potential. It is possible therefore that the BWS, with their high iron content play a role in sludge formation. The results of this investigation were inconclusive because of the presence of varying amounts of more hydrophobic solids as contaminants in the BWS samples separated. However, in some of the trials conducted a significant increase in some sediment volume was noted after treatment. The implication of these results is that the BWS solids could be involved in sludge formation either as a primary or secondary structure.

INTRODUCTION

The Hot Water Extraction Process (HWEP) used by Suncor and Syncrude to extract bitumen from the Athabasca oil sands produces tailings with about 35 % more volume than that occupied by the bituminous sands before mining. This increase is largely the result of water hold-up in the fines fraction from the tailings, arising primarily from the `middlings' treatment circuit. Long term economical and environmentally acceptable operation of this process ideally depends on being able to reduce the tailings volume. Therefore, economical reduction of the water content of tailings fines is of critical interest.

In our previous work, we have investigated the applications of oil-phase agglomeration techniques for the removal of residual organics and oil wettable solids from the aqueous tailings streams of bitumen separation plants.[1-3] This treatment results in destabilization of the sludge which then differentiates into four distinct layers: clear water, a colloidal suspension a thin dark brown interface layer and a well compacted sediment. The colloidal fraction displays a propensity to form gels which are believed to be largely responsible for the water holding capacity of sludges.[4] The solids in the brown interface layer have a relatively high carbon content compared to the other solids fractions. This organic matter is insoluble in toluene and has been designated as, "strongly bound organic matter, SOM". These organic rich solids could also play a significant role in the formation of sludge structure because they are wettable by both oil and water, that is they have a bi-wetted surface, hence the designation BWS. The BWS could be capable of forming a strongly flocculated structure through interaction with the, free bitumen and naphtha present in sludge.

In this investigation changes in sediment volume for BWS, in the presence of bitumen and naphtha, have been used as a measure of flocculation. The results are expected to be of some help in the understanding of the role of BWS in the stability of sludge structure.

EXPERIMENTAL METHODS

Sample description. Aqueous sludge from the 17m level of the Syncrude tailings pond was pumped into 200 L plastic drums[5]. Each drum was inverted five times (with a barrel tipper) before being divided among a number of 5 L plastic jugs, which were then stored in a cooler at 10 C. The results presented in this report were obtained on these sub-samples, provided courtesy of R. Schutte of Syncrude Canada Ltd. Before further sub-sampling, each jug was shaken vigorously by hand to ensure thorough mixing. The physicochemical properties of sludge, provided by Syncrude, are presented in Table 1[6]

Table 1.Physicochemical properties of Syncrude Sludge

Property	Value
pH at 17.8±0.5 C	7.83±0.03
Conductivity (ms/cm)	1.6±0.01
Total Solids [Gravity] ,wt. %	26.6±0.1
Bitumen [OWS] ,wt. %	0.9±0.05 (1.1±0.2)
Solids [OWS] ,wt. %	25.6±0.1 (26.5±0.9)
Density (calculated) ,g/ml	1.19
Solids ,< 44μ (%)	99.2±1.0
Solids ,< 22μ (%)	94.9±1.9
Solids ,< 11μ (%)	83.7±2.1

Values in parenthesis were determined at NRC.

Separation of Bi-wetted solids

Procedure 1. A 500g sample of sludge was gently agitated with 2mm size teflon balls in a polyethylene bottle on a roller mill to remove residual bitumen along with its associated hydrophobic solids. The cleaned sludge was agitated for 30 minutes on a paint shaker and then centrifuged at 200 X g for 30 minutes. The sediment from centrifugation was transferred to a Waring Blendor jar using pond water. The contents were agitated at 10000 rpm for 10-15 minutes to produce a large volume of stable foam. The foam was separated and the remaining suspension agitated again. This procedure was repeated several times until the colour of the foam changed from brown to grey. The foam was washed several times with pond water to remove any inert solids by differential settling. The settlted solids were labelled BWS-1. A portion of BWS-1 was cetrifuged at 100 X g for 5 minutes and then dried in an oven at 110 C prior to carbon determination using a Leco CR12 carbon analyzer. The remainder was kept as an aqueous slurry for sedimentation studies. The loss in weight on drying of the centrifuged sample was used for the determination of water content of the centrifuged cake. Two additional samples of BWS were prepared using this procedure, except that the solids were washed with distilled water instead of pond water. These samples were labelled BWS-2 and BWS-3.

Procedure 2. A 500g of sludge was gently agitated with stainless steel balls in a polyethylene bottle on rollers in order to collect remove residual bitumen and hydrophobic solids as a surface coating on the balls. The clean sludge was then agitated in a Waring Blendor to collect foam as described in Procedure 1. Inert solids were washed out of the foam using distilled water. The slurry, containing clean BWS, was then centrifuged at 100 X g for 5 minutes. This procedure resulted in two sediment layers which were separated using a spatula. The top layer was given the designation fine bi-wetted solids (FBWS), while the bottom layer was described as coarse bi-wetted solids (CBWS). A summary of the analytical data for BWS samples is given in Table 2.

Table 2. Summary of analytical data for BWS

Sample ID	**C, Wt.%**	Average particle size,µm	Water content of centrifuged cake, Wt.%
BWS-1	15.5	16.1	122
BWS-2	13.0	12.6	114
BWS-3	14.9	17.8	120
FBWS	17.8	6.4	141
CBWS	21.0	24.0	139

Flocculation Test. A 15 ml sample of a slurry containing about 30 wt.% of BWS was transferred to a 100 ml glass jar. A small amount of 60 wt.% bitumen solution in Stoddard solvent was added to this slurry which was then diluted to 30 ml with pond water. The jar was sealed with a polyethylene gasket and then agitated for 5 minutes on a Spex mixer. The contents of the jar were transferred to a preweighed 50 ml graduated glass cylinder, using pond water washings to make up the volume. The sedimentation volume of the BWS was noted visually from the cylinder markings, readings were taken after the suspension had been allowed to settle under gravity for 96 hours, although little change was observed after 4-6 hours. The supernatant from the cylinder was decanted off after noting down the final sediment volume. The jar containing wet, sediment was then weighed and the contents dried to determine the true weight of BWS used. Corrections were applied for the weight of added bitumen.

Analysis of Bi-Wetted Solids. Scanning electron micrographs of the solids were recorded using a JEOL model JSM-5300 instrument operated at 10 kV. The samples were coated with a thin layer of carbon to impart conductivity. Energy dispersive X-ray analysis was performed with a Link model QX2000 system attached to the scanning electron microscope.

Flocculation of Sub-bituminous Coal. For comparison purposes a sample of sub-bituminous coal was treated in the same way as the BWS, except that both water and Stoddard solvent as well as bitumen solution in Stoddard solvent were used as flocculating agents.

RESULTS AND DISCUSSION

Five samples of BWS were separated from Syncrude sludge pond tailings. The carbon content and the average particle size of these samples varied considerably, probably as a result of different amounts of "contaminants" (inert and hydrophobic solids) associated with these materials. In general a higher carbon content is associated with more hydrophobic behaviour. Energy dispersive X-ray analysis (EDXA) indicate that all of the samples were chemically similar. The main elements were Al and Si with small amounts of Fe, Ti, Cu and S. However, the distribution of Fe appeared to be non-uniform. Scanning electron micrographs, (SEM) of the samples were also similar and indicated plate- like particle shape, but with particle sizes ranging from 1-10μm. All samples appeared to have a coating of an amorphous non-conducting material which volatilized on the passage of the electron beam.

Structure Forming Propensity

An oil phase agglomeration technique was used to study the flocculation characteristics of BWS. The form of the agglomerated material is critically dependent on the amount of bridging (or bindind) liquid used, the degree and type of agitation and the wetting properties of the material.[7,8] For example, voluminous clusters of flocs result when a small amount of bridging liquid is employed, causing a large increase in of Fe, Ti, Cu and S. However, the distribution of Fe appeared to be non-uniform. Scanning electron micrographs, (SEM) of the samples were also similar and indicated plate-like particle shape, but with particle sizes ranging from 1-10μm. All samples appeared to have a coating of an amorphous non-conducting material which volatilized on the passage of the electron beam.

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The sedimentation behaviour of BWS after agitation with varying amounts of 60 wt.% bitumen solution in Stoddard solvent is illustrated in Figures 2 to 6. These figures show the sedimentation volume of the BWS as a function of added bridging liquid (bitumen). The results were non-reproducible and therefore inconclusive. The sedimentation volume of BWS-1 first increased, then decreased before finally increasing again. The initial addition of bitumen resulted in the formation of flocs, accounting for the higher sediment volume obtained. On further addition of bitumen some compact agglomerates may have formed resulting in a lower sediment volume. The second increase in volume is not completely understood at this time. It is possible that the BWS fractions separated are in fact a mixture of solids covering a range of hydrophobicity. The observed behaviour might then represent a two stage process in which the more hydrophobic solids first agglomerate to give a decrease in sediment volume followed by an increase resulting from flocculation of a less hydrophobic fraction.

The quantity of BWS-2 was only sufficient to carry out three tests. It is seen from Figure 3 that in this case successive additions of bitumen result in only an increase of the settled volume of BWS-2. This fraction had the lowest carbon content of all those studied. The BWS-3 sample shows yet another relationship, relative to the amount of bitumen added. With the first addition of bitumen, the sedimentation volume of BWS-3 decreases but on further additions the volume increases (Figure 4). Again this behaviour could be explained on the basis of the fraction being a mixture of solids with different hydrophobicities. Figure 5 is a plot of the change in the sediment volume of BWS-3 as a function of the change in bitumen volume added. The data has been plotted as a least squares fit with a correlation coefficient of 0.991. The plot indicates that the observed sediment volume increase, after the initial sharp drop, cannot be totally explained by the increase in bitumen added, ie. the sediment volume increase is almost four times the volume of added bitumen. This indicates that some structure change in the sediment has in fact occurred.

The sedimentation behaviour of fine and coarse BWS samples shown in Figure 6 is typical of the formation of compact agglomerates on successive additions of bitumen. This is consistent with their high carbon contents relative to the other samples.

Figures 7 and 8 demonstrate the effect of bitumen on the retention of water by the settled BWS sediment. The behaviour of FBWS and CBWS is consistent with the displacement of water by successive additions of bitumen. However, the behaviour of the other three samples of BWS is more complex.

flocs), whereas subsequent additions result in flocculation of the mineral matter associated with the coal.

CONCLUSIONS

The results of preliminary tests on the agglomeration behaviour of bi-wetted solids by bitumen are inconclusive. The presence of varying amounts of more hydrophobic solids as contaminant complicates the results. However, the results demonstrate that the biwetted solids are capable of being flocculated with bitumen and/or naphtha to give a significant expansion in sediment volume.

FURTHER WORK

Further work will concentrate on the efforts to modify the fractionation scheme in order to separate cleaner fractions of bi-wetted solids, before investigating their wetting characteristics by oil phase agglomeration technique.

ACKNOWELDGEMENTS

Preliminary work for the preparation of bi-wetted solids was carried out by Mr. Will Green a summer student from Victoria University.

LIST OF ABBREVIATIONS

Abbreviation	Explanation
BWS	Bi-wetted solids
FBWS	Fine Bi-wetted solids
CBWS	Coarse Bi-wetted solids
SOM	Strongly Bound Organic Matter
HWEP	Hot Water Extraction Process
OWS	Oil Water Solids Analysis
SEM	Scanning Electron Micrographs
EDXA	Energy dispersive X-ray Analysis

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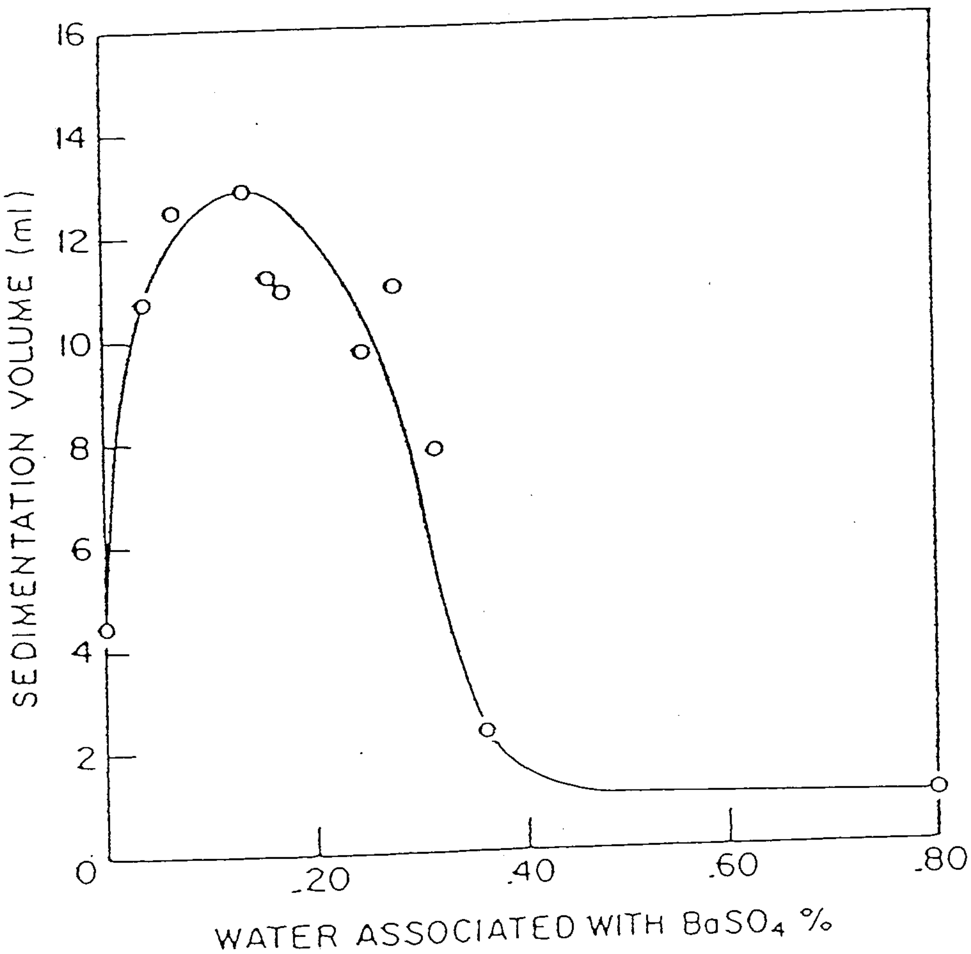

IG. 1. The effect of water on the sedimentation volume of barium sulphat

Fig. 2. The effect of bitumen additionon the sedimentation volume of BWS-1 sample dispersed in pond water

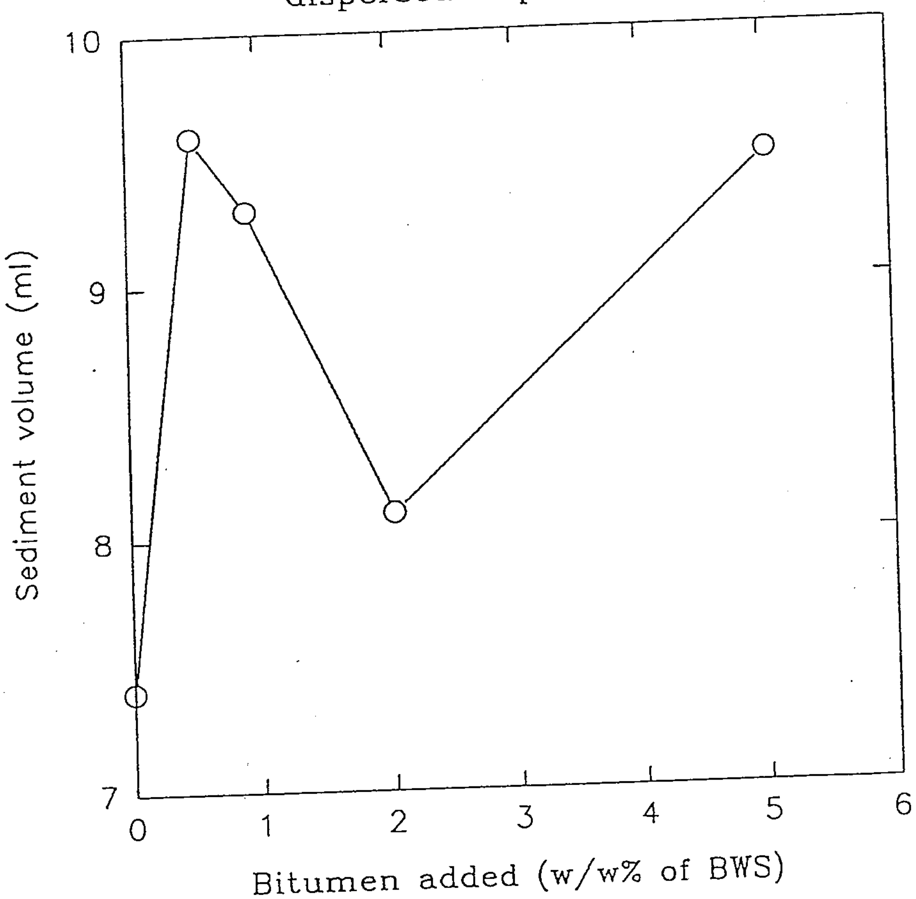

Fig. 4. The effect of bitumen additionon the sedimentation volume of BWS-3 sample dispersed in pond water

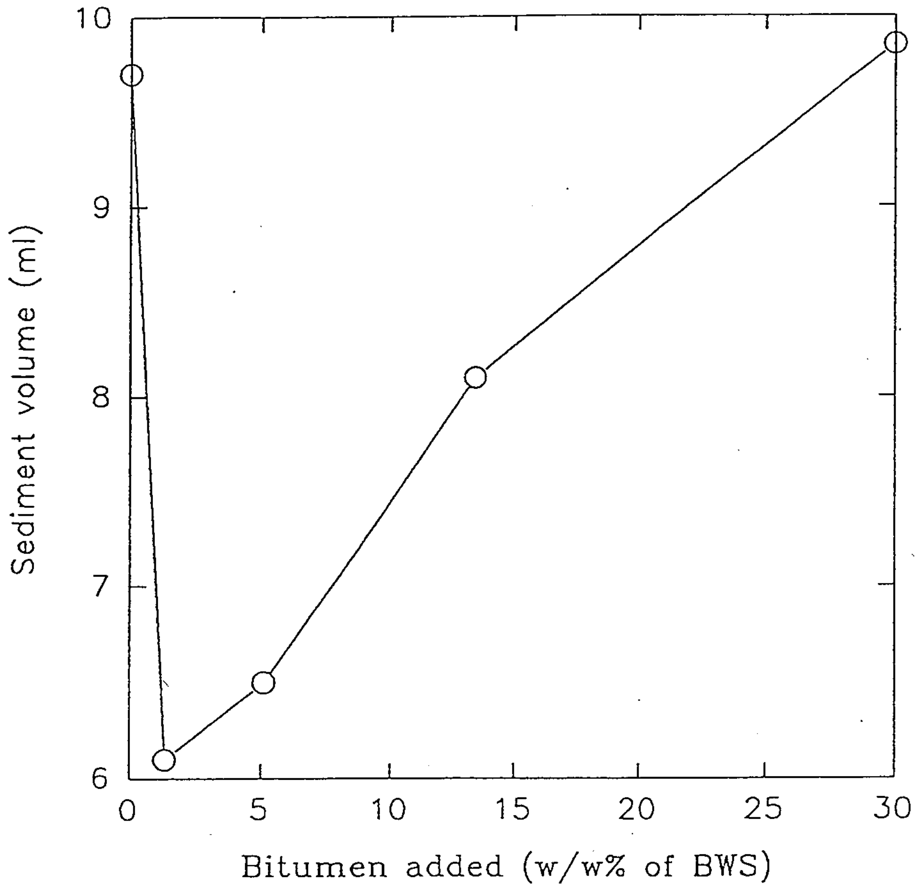

Fig. 3. The effect of bitumen additionon the sedimentation volume of BWS–2 sample dispersed in pond water

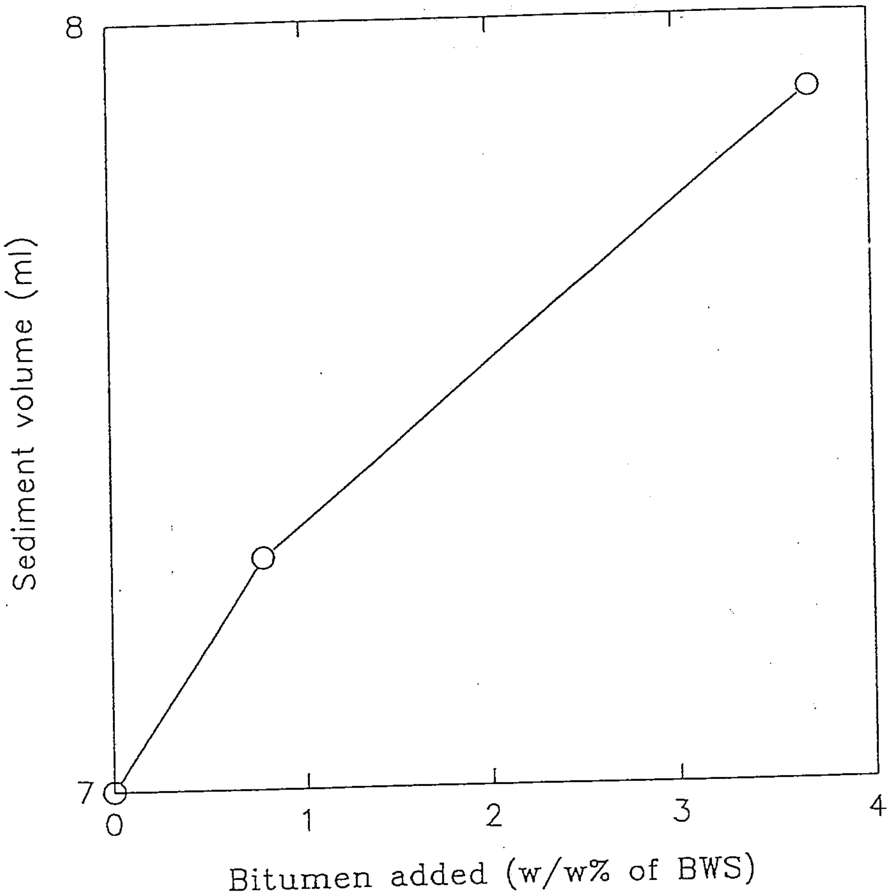

Fig. 6. The effect of bitumen on the sedimentation volume of BWS dispersed in pond water

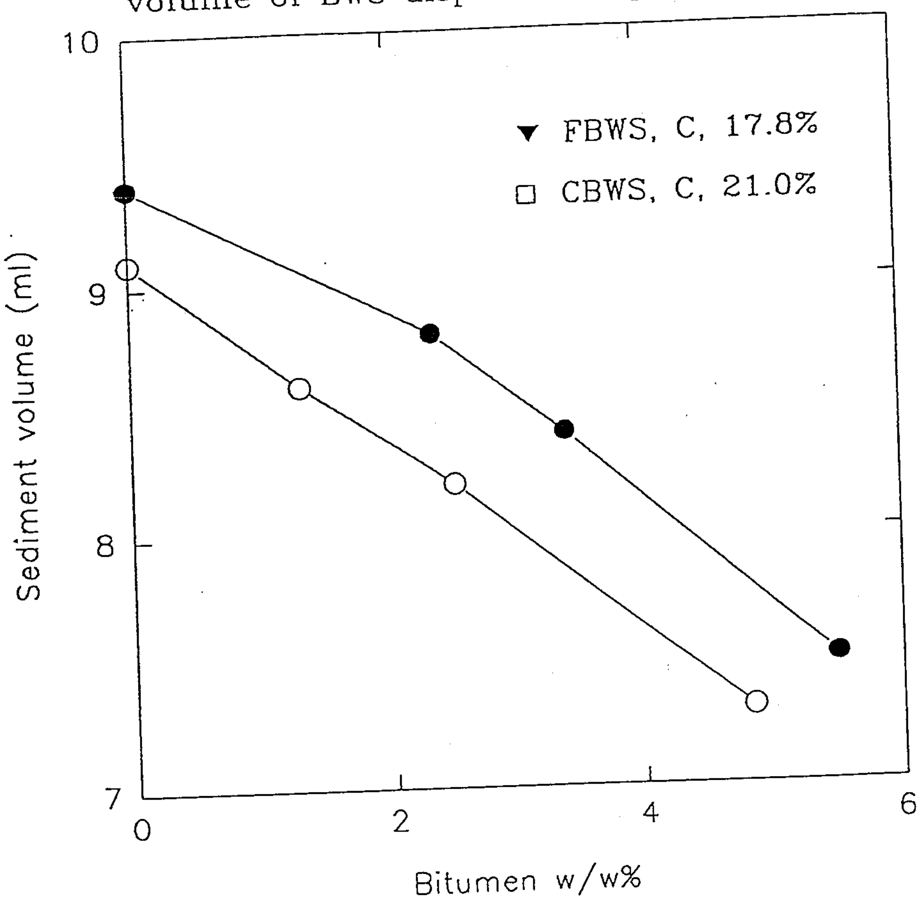

Fig. 5. Effect of the variation in the volume of bitumen on the sediment volume of BWS-3

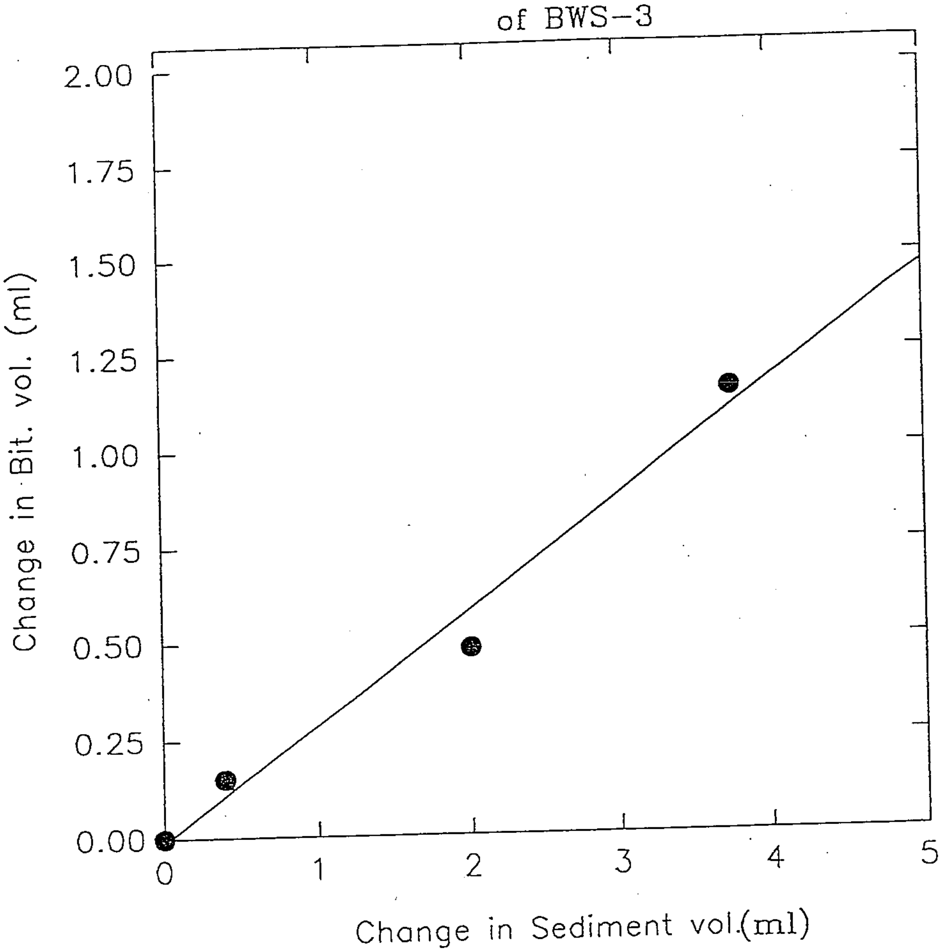

Fig. 8. Effect of bitumen on the water content of BWS-3 (Carbon content, 14.9%)

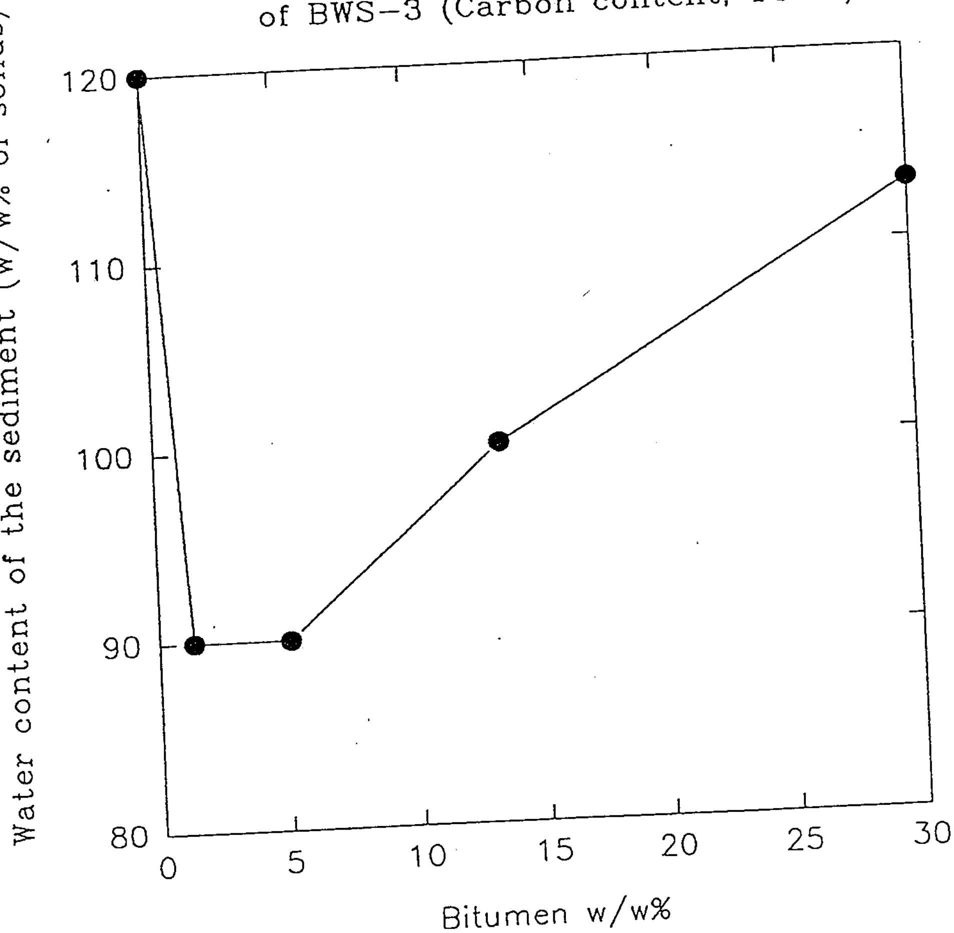

Fig. 7. Effect of bitumen on the water content of sediment

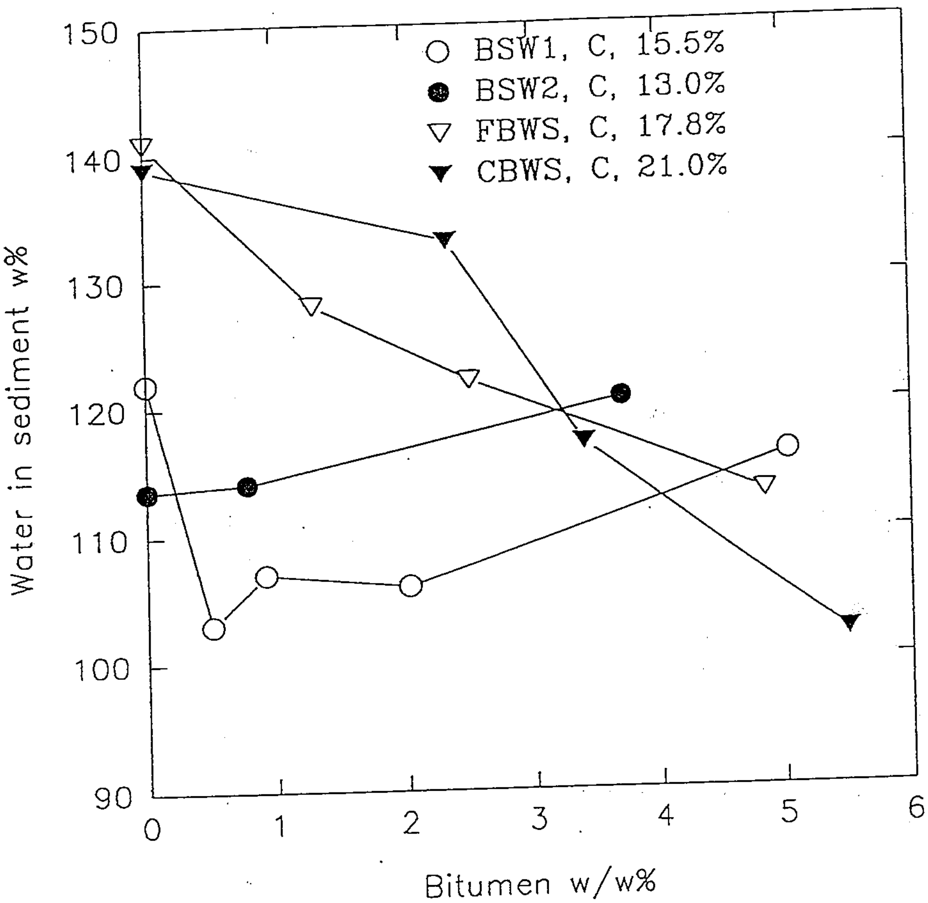

Fig. 9. The effect of bridging liquid (varsol) on the final sedimentation volume of Subbitumonous coal

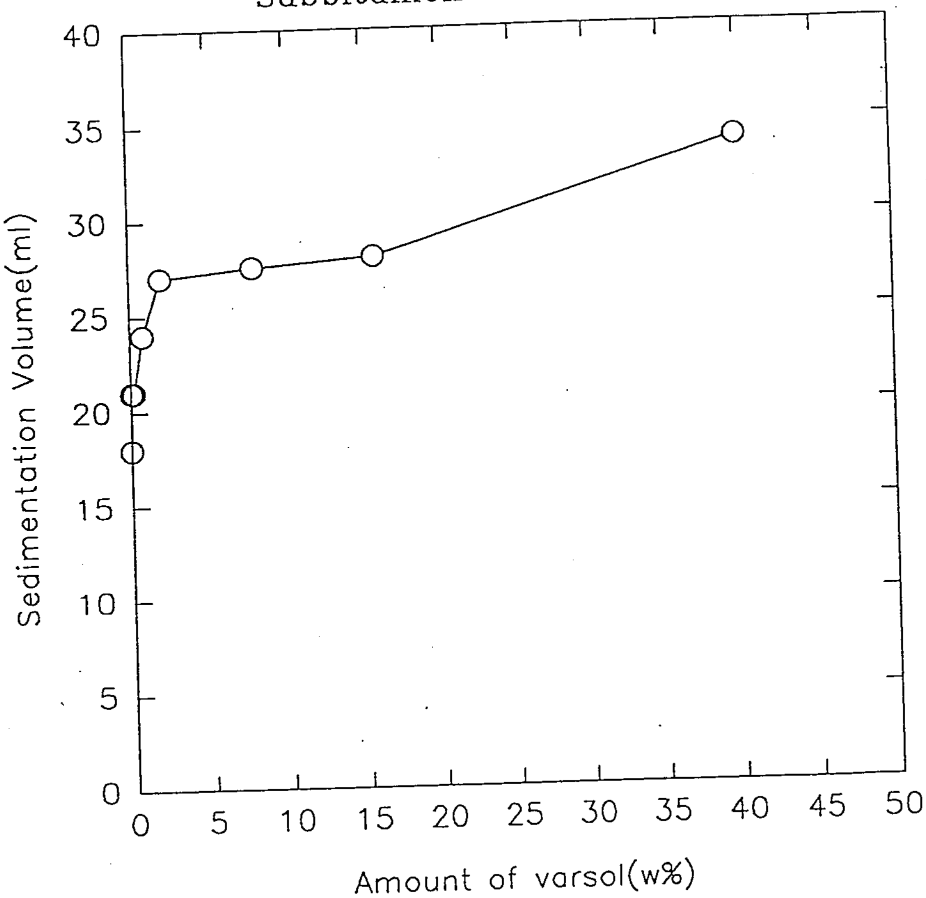

Fig. 9. The effect of bridging liquid on the sedimentation volume of subbituminous coal

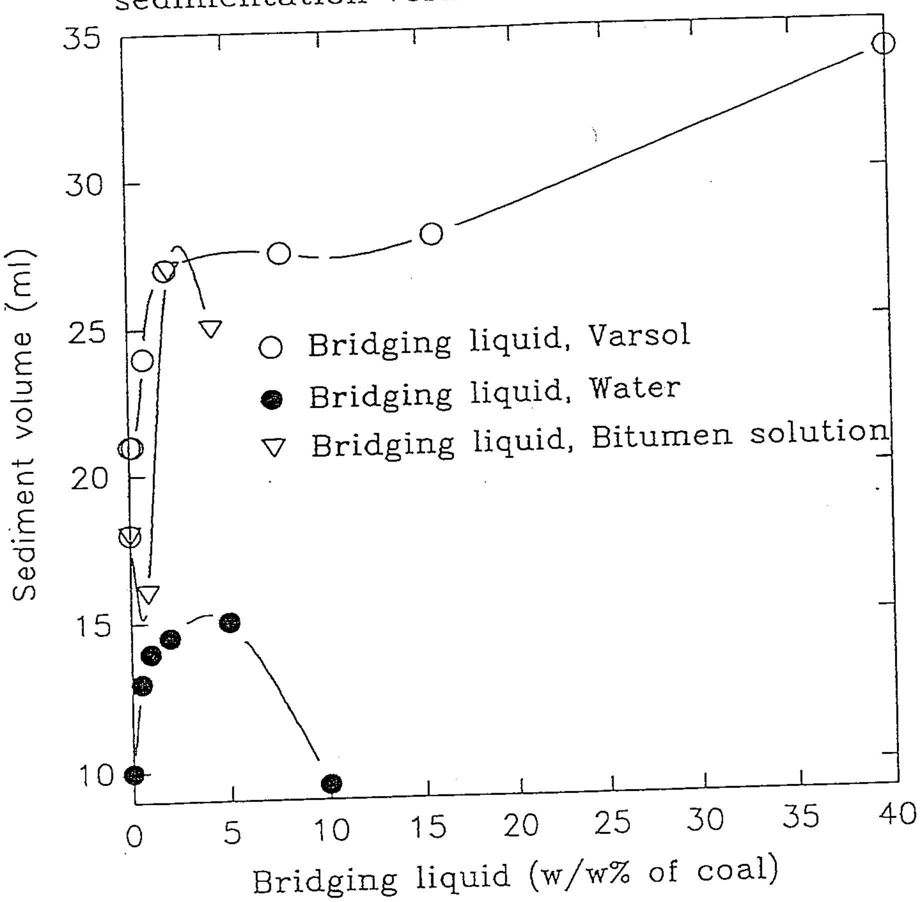

Fig. 11. The effect of bridging liquid (60% bitumen solution in varsol) on the sedimentation volume of subbituminous coal

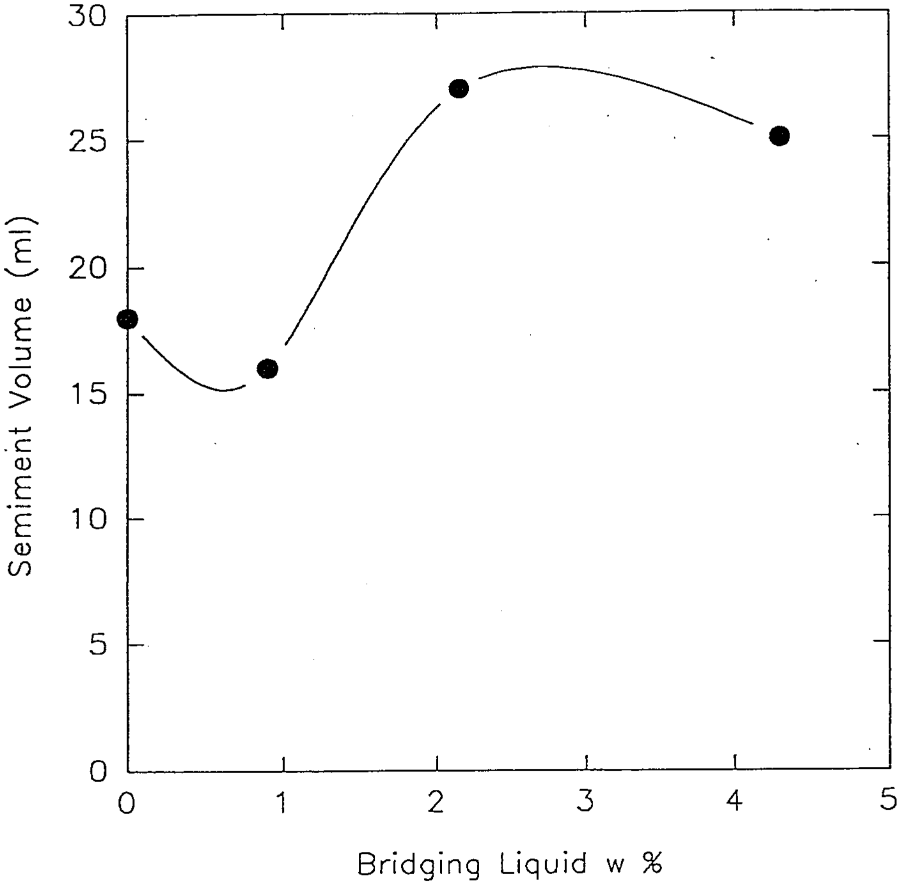

Fig. 10. The effect of water on the sedimentation volume of a subbituminous coal dispersed in varsol

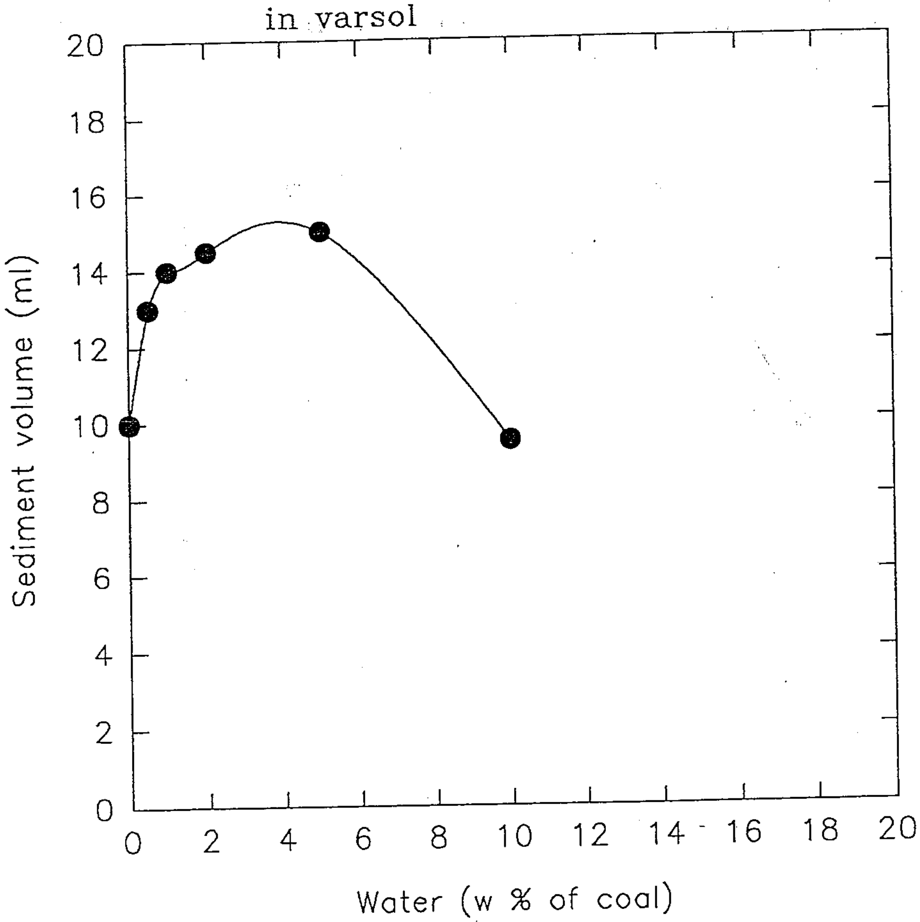

Fig. 11. The effect of bridging liquid (60% bitumen solution in varsol) on the sedimentation volume of subbituminous coal