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THE INFLUENCE OF SODIUM DITHIONITE ON FLOTATION OF PYRITE AND COAL WITH DIESEL FUEL

The effect of sodium dithionite ($Na_2S_2O_4$) - a reducing agent - was investigated on microflotation of pyrite and two american coals of different hydrophobicity (Lower Kittanning and Upper Freeport) with diesel fuel as a collector. It was shown that both collectorless and diesel fuel flotation of hydrophobic, sulphurized pyrite as well as diesel fuel flotation of untreated pyrite essentially decreased in the presence of sodium dithionite in the flotation pulp. Flotation tests performed with 1.40 float and 1.80 sink fractions of examined coals indicated the improvement in flotation recovery of 1.40 float fraction and decrease in recovery of 1.80 sink fraction for relatively more hydrophobic, Upper Freeport coal. There was no influence observed of reducing agent on the floatability of both gravity fractions for hydrophilic, Lower Kittanning coal.

INTRODUCTION

The separation of coal and pyrite by froth flotation has been a difficult problem for a long time (Wheelock, Markuszewski, 1984). The rejection of pyritic sulphur and ash forming minerals from run of mine coal, prior to the combustion or another technological destination, appeared to be one of the most important tasks, mainly due to its environmental meaning.

Flotation is the most effective methods of separation of carbonaceous and mineral matters of coal. In order to enhance the selectivity of flotation different pretreatment methods can be used which increase the hydrophobicity of coal and decrease the hydrophobicity of the mineral fraction (Capes et al., 1973; Arnold and Aplan, 1990). The application of reducing agents seems to be one of the most promising ways improving the separation of coal organic matter and

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mineral matter, including pyrite. The influence of sodium dithionite ($Na_2S_2O_4$), a reducing agent, on grinding and subsequent beneficiation of different coals was studied by Birlingmair and co-workers (Birlingmair et al., 1988, 1989). They showed that dithionite improves flotation recovery of coal. The observed advantageous influence of dithionite on the separation of combustible, organic coal fraction and the ash forming minerals was explained as the result of reduction process taking place on the mineral and coal surfaces. They postulated that the improved separation resulted from the increase in floatability of coal fraction and the decrease in floatability of pyrite and ash forming minerals.

The purpose of this work is the examination of influence of sodium dithionite - a reducing agent on the beneficiation of coal by flotation. Model microflotation experiments in modified Hallimond tube were performed for pyrite and two coals of different hydrophobicity: Lower Kittanning (relatively hydrophilic coal) and Upper Freeport (relatively hydrophobic coal). Diesel fuel, commonly used in coal flotation practice, has been applied as a flotation collector.

EXPERIMENTAL

Materials

Sulphurized mineral pyrite (Huanzala, Peru) which was treated with aqueous sodium sulphide and then oxidized to create the hydrophobic layer of elemental sulphur (Drzymała et al., 1990) was used in microflotation experiments. To avoid the mechanical carry-over of pyrite, greater than 61 μm pyrite particle were used in the flotation tests. The maximum size of entrained pyrite particles (D_{max}) was calculated from the flotometric equation: $D^M_{max} < L^M 1/(\rho_p - \rho_v)$. For our Hallimond tube the L^M value is equal to 0.029 ± 0.007 g/cm^2 (Drzymała et al., 1990), ρ_p and ρ_v are the particle density and water density, respectively. The size fraction of +250-350 μm was selected for experiments.

Two american coals: Lower Kittanning coal and Upper Freeport coal were used in the microflotation tests. The coals were selected due to their different hydrophobicity. The Upper Freeport coal is known as a more hydrophobic than the Lower Kittanning coal (Birlingmair et al., 1988, 1989).

The samples were crushed, ground, and then, desired particle size fractions were separated by means of dry screening. Coal samples were subsequently separated by means of Certigrav into two specific gravity fractions: 1.40 float and 1.80 sink, dried at 85°C and stored in sealed jars. To minimize the mechanical carryover of particles during flotation, the particle sizes used for flotation tests were: +600-850 μm for 1.40 float fraction and +150-250 μm for 1.80 sink fraction. The ash and sulphur content for particular specific gravity fractions are given in Table 1.

Table 1.

Moisture free ash and sulphur contents for 1.40 float and 1.80 sink coal fractions for Upper Freeport and Lower Kittanning coals.

UPPER FREEPORT COAL

GRAVITY FRACTION	ASH, %	SULPHUR, %
1.40 float	5.81	1.15
1.80 sink	75.50	5.93

LOWER KITTANNING COAL

GRAVITY FRACTION	ASH, %	SULPHUR, %
1.40 float	6.18	1.76
1.80 sink	75.11	6.87

According to the data given in Table 1, the 1.40 float fractions are predominantly represented by organic matter, whereas 1.80 sink fractions are predominantly represented by pyrite and ash forming minerals.

Microflotation experiments.

Microflotations were conducted in the multi-bubble Hallimond tube equipped with a calibrated receiver enabling continuous measuring of the recovery of floating particles in the course of an experiment. A one gram sample of either coal or sulphurized pyrite was placed in the base of the Hallimond tube and conditioned for 5 minutes in 50 ml of distilled water and a proper amount of diesel fuel collector was introduced to the flotation cell in the form of previously prepared oil/water emulsion. After conditioning, water was added to attain 150 ml of mixture.

Flotation was initiated using nitrogen at a flow rate of 30 ml/min. Both the nitrogen flow rate and the stirring speed were kept constant in all flotation tests. Microflotation tests were conducted either at natural pH and redox potential or at the potential created by sodium dithionite ($Na_2S_2O_4$) introduced into the flotation slurry as a reducing agent. The redox potential measured by means of platinum electrode in the Hallimond tube was - 0.51 V (SCE) for $2x10^{-2}$ M $Na_2S_2O_4$, whereas the potential of pyrite electrode was within the range from -0.44 to -0.47 V(SCE) for the $Na_2S_2O_4$ concentration ranging from $5x10^{-4}$ to $2x10^{-2}$ M (Chmielewski, 1990). While sodium dithionite was applied, the Hallimond tube was kept closed to the atmosphere to avoid the oxidation of

$Na_2S_2O_4$. Sodium sulphate (Na_2SO_4) was also used in some tests to maintain a constant ionic strength when results were compared to those observed in the presence of the reducing agent.

RESULTS AND DISCUSSION

Pyrite.

The pyrite fraction of +250-300 μm used in experiments presented in Fig.1 was non-floatable during collectorless flotation, while a very efficient collectorless flotation and flotation with diesel fuel collector was induced when pyrite particles were sulphurized, that is coated with thin layer of elemental sulphur. The sulphurization leads to the formation of thin, hydrophobic layer of elemental sulphur in the heterogenic, electrochemical reaction of oxidation of H_2S or HS^- by oxygen on the pyrite surface (Hamilton and Woods, 1981, 1984; Heyes and Trahar, 1984; Walker and Walters, 1986) The flotation of such pyrite appeared to be very effective (Fig.1). However, when sulphurized, hydrophobic pyrite particles were conditioned in the solution of reducing agent - $Na_2S_2O_4$ - we subsequently observed very pronounced decrease in pyrite recovery. According to Fig.1, 5 min. conditioning of sulphurized pyrite with 0.01 M aqueous $Na_2S_2O_4$ and subsequent flotation with diesel fuel (1 mg/g FeS_2) reduce significantly pyrite recovery. Such behavior of pyrite being in contact with aqueous sodium dithionite can be explained on the basis of electrochemical properties of

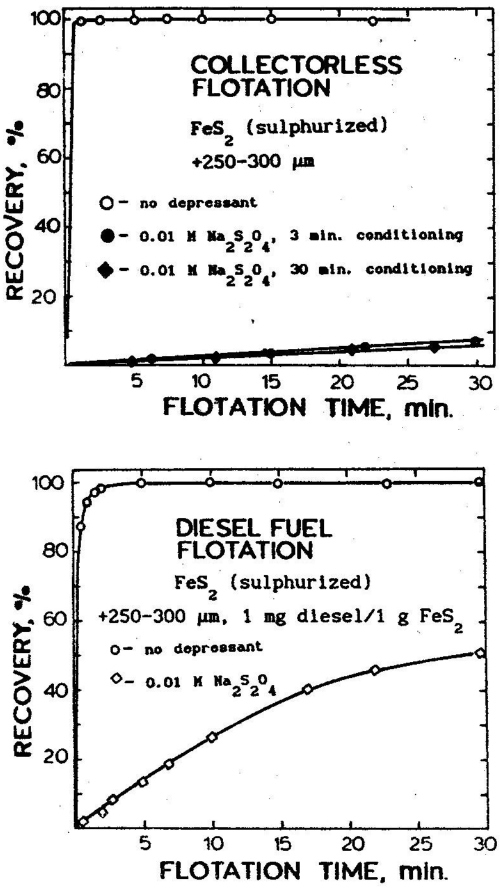

Fig.1.
The effect of sodium dithionite ($Na_2S_2O_4$) on the collectorless and diesel fuel flotation of sulphurized pyrite.

pyrite. Pyrite electrodes exhibits very low potential in sodium dithionite solutions (Chmielewski, 1990) which corresponds to the reduction of pyrite oxidation products and cathodic decomposition of pyrite itself (Heyes and Trahar, 1984; Hamilton and Woods, 1981). Therefore, we also expect that conditioning of sulphur-coated, hydrophobic pyrite particles in dithionite containing slurries leads to the cathodic reduction of elemental sulphur layer. This results in decrease of pyrite hydrophobicity as well as in collector adsorption on pyrite surface. Consequently, the observed flotation of pyrite became very poor. The depressing effect of sodium dithionite was also confirmed in flotation of untreated pyrite with diesel fuel within the wide range of the collector concentration (0.04 - 50 mg/g FeS$_2$) (Fig. 2). An evident decrease in recovery of pyrite was observed both after 10 minutes and after 30 minutes flotation.

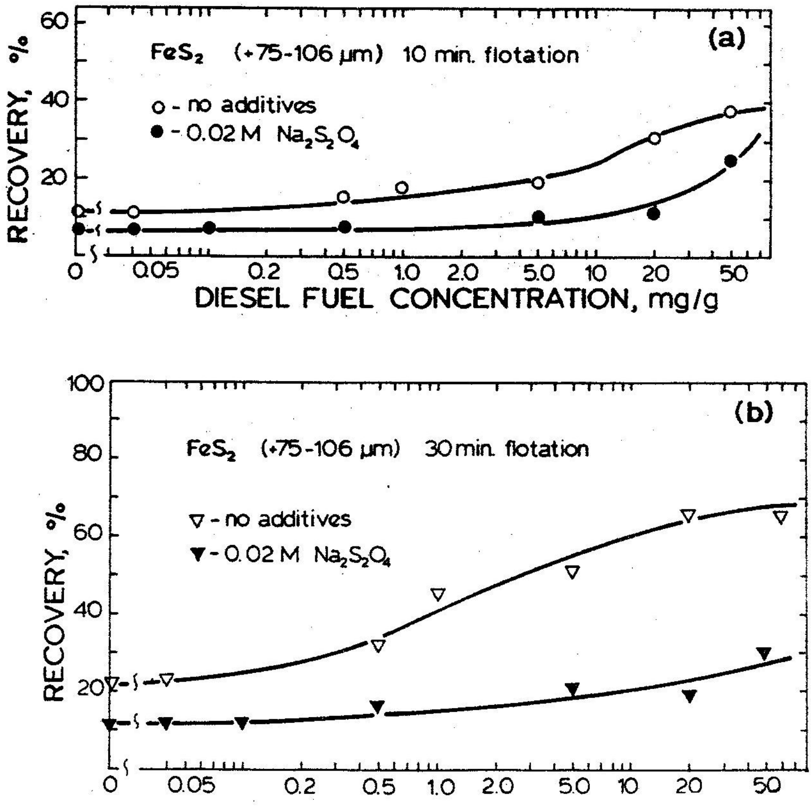

Fig. 2.
The effect of sodium dithionite on the diesel fuel flotation of untreated pyrite after 10 (a) and 30 (b) minut. of flotation.

Lower Kittanning coal.

A significant increase in flotation of Lower Kittanning 1.40 float fraction was observed (Fig. 3) when concentration of the collector exceeded 0.1 mg/g of coal. The flotation experiments performed in the presence of either 0.02 M sodium sulphate or 0.02 M sodium dithionite indicated a negligible effect of these additives on the flotation results. Microflotations of the Lower Kittanning 1.80 sink fraction (Fig. 3) exhibited an increase in the recovery when sodium sulphate was introduced to the flotation slurry. This increase could be most likely a result of increasing ionic strength (salt effect). When sodium dithionite - a reducing agent - was introduced, the recovery decreased in comparison to that in the presence of sodium sulphate of the same ionic strength. Basing on the results observed for Lower Kittanning coal, we could not expect a substantial improvement of selectivity of diesel fuel flotation of organic and mineral fractions by application $Na_2S_2O_4$, a reagent which lowers redox potential during flotatien.

A comparison of the flotation results for both coal gravity fractions at different diesel concentrations (Fig. 3) indicates the possibility of selective separation of coal and pyrite with ash forming

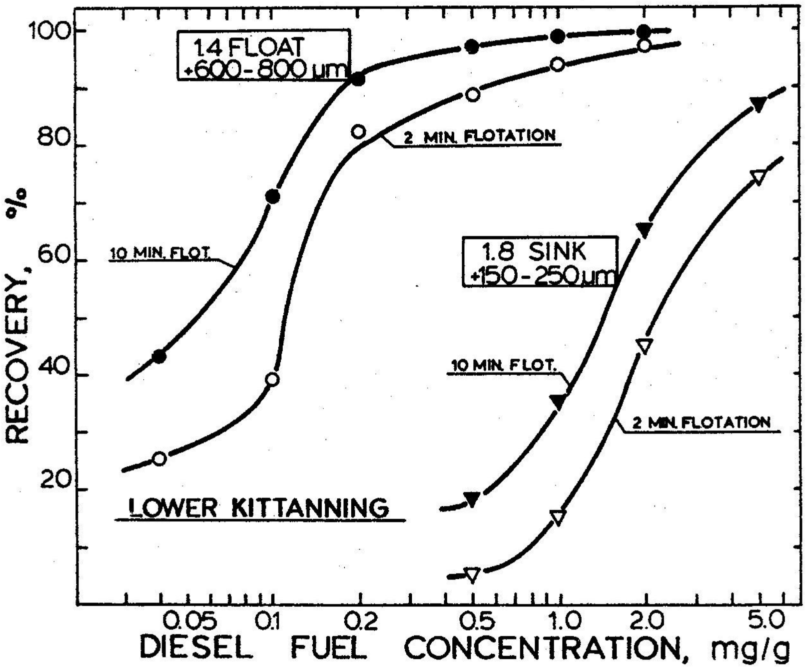

Fig. 3.
Comparison of floatabilities of 1.40 float and 1.80 sink fractions of Lower Kittanning coal with diesel fuel of different concentrations.

minerals, when the concentration of the collector is kept in the range of 0.2 - 0.5 mg/g of coal, i.e. at maximum floatability of the carbonaceous matter and minimum floatability of the mineral fraction. Therefore, the application of suitable concentration of diesel fuel collector, rather than the presence of reducing agent, enhances selective separation of mineral and organic fractions of the Lower Kittanning coal.

Upper Freeport coal.

The recovery vs. collector concentration plots, given in Fig.4, confirm a better floatability of Upper Freeport coal than that of Lower Kittanning coal. Very efficient flotation of 1.40 float fraction was already observed at diesel fuel concentration of 0.1 mg/g of coal. In contrast to the Lower Kittanning coal (Fig.3), the separation of the ash-forming minerals from coal was non-selective at all fuel oil concentrations tested (Fig.4). At the collector concentration of 0.5 mg/g coal, both fractions of Upper Freeport coal were observed to float very effectively.

Microflotation test with diesel fuel collector performed in 0.02 M $Na_2S_2O_4$ aqueous solution (not shown here) indicated some beneficial

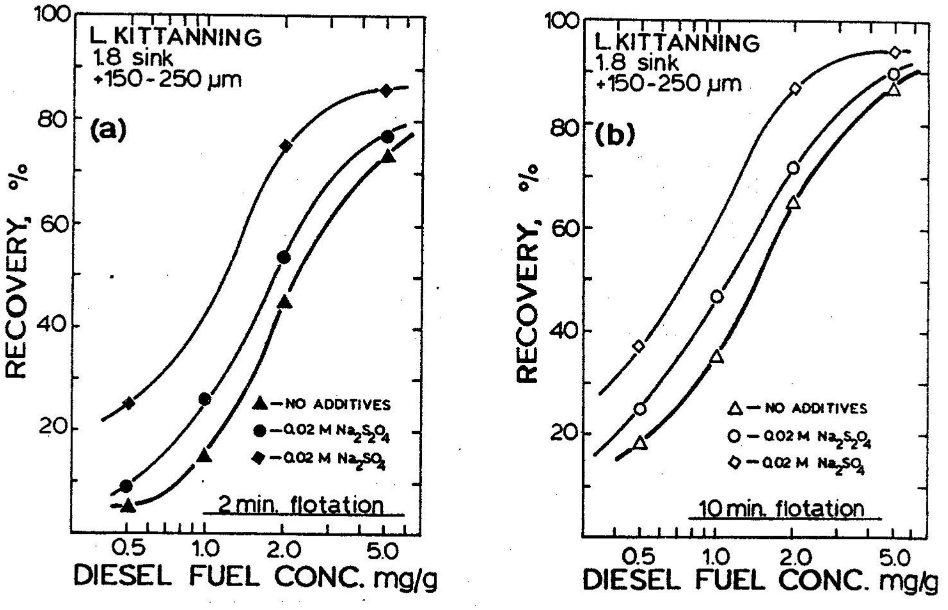

Fig. 4.
Recovery - diesel fuel concentration plot for 1.80 sink fraction of Lower Kittanning coal after 2 minutes (a) and after 10 minutes (b) of flotation.

effect of dithionite on the flotation recovery of 1.40 float fraction. Flotation of the 1.80 sink fraction (Fig.6) decreases only when sodium dithionite is introduced to the flotation cell. Therefore, one can expect a significant improvement in selectivity of separation of pyrite and ash forming minerals from coal if sodium dithionite is added in flotation of the Upper Freeport coal. Fig.5 in the form of the recovery - collector concentration relationships shows that such an improvement could not be observed without the dithionite.

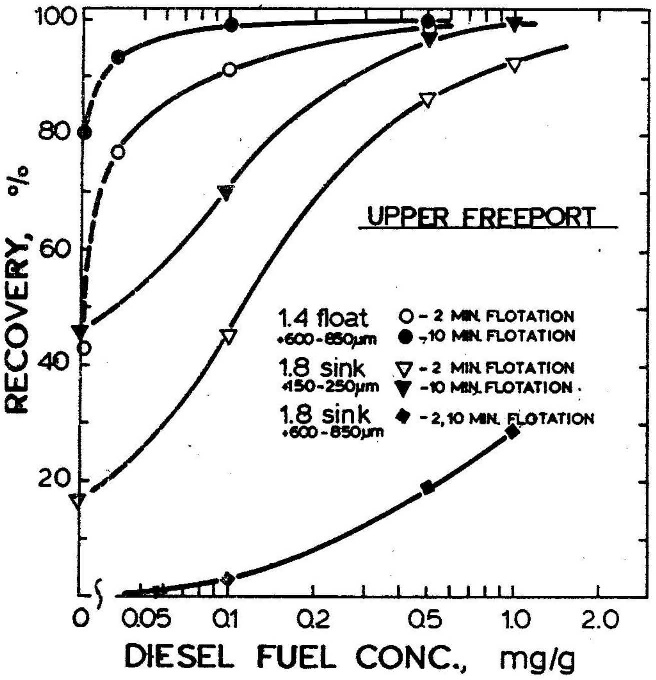

Fig.5.

Comparison of floatabilities of 1.40 float and 1.80 sink fractions of Upper Freeport coal with diesel fuel of different concentrations.

CONCLUSIONS

Sodium dithionite is a very effective depressing agent in flotation of pyrite. The depressing action of the additive was evident both in the collectorless flotation of hydrophobic, sulphurized pyrite, and flotation of untreated pyrite with diesel fuel. We postulate that the essential depression of sulphurized pyrite, when sodium dithionite was was added to the slurry, results from electrochemical reduction of hydrophobic sulphur on the pyrite surface. Dithionite is an effective depressant of hydrophobic pyrite particles and its advantageous influence can be utilized in improving the selectivity of separation of pyrite from coal by flotation. In the case of coal the promoting role of the reducing agent is not univocal and requires separate tests for each type of material.

Microflotation experiments with the organic (1.40 float) and mineral (1.80 sink) fractions of Lower Kittanning and Upper Freeport coals with diesel fuel as the collector showed that the selectivity of separation can be influenced either by the application of an appropriate concentration of the collector (Lower Kittanning coal) or by the introduction of sodium dithionite (Upper Freeport coal). A selective removal of pyrite and ash forming minerals from relatively hydrophilic, Lower Kittanning coal is expected to be effective when the concentration of diesel fuel does not exceed the range of 0.2 - 0.5 mg/g coal. The application of dithionite did not influence the flotation selectivity.

Flotation recoveries of both organic and mineral fractions of Upper Freeport coal increased significantly when the concentration of diesel fuel was above 0.05 mg/g coal. Therefore, an attempt to clean these two fractions by application of an optimum concentration of the collector

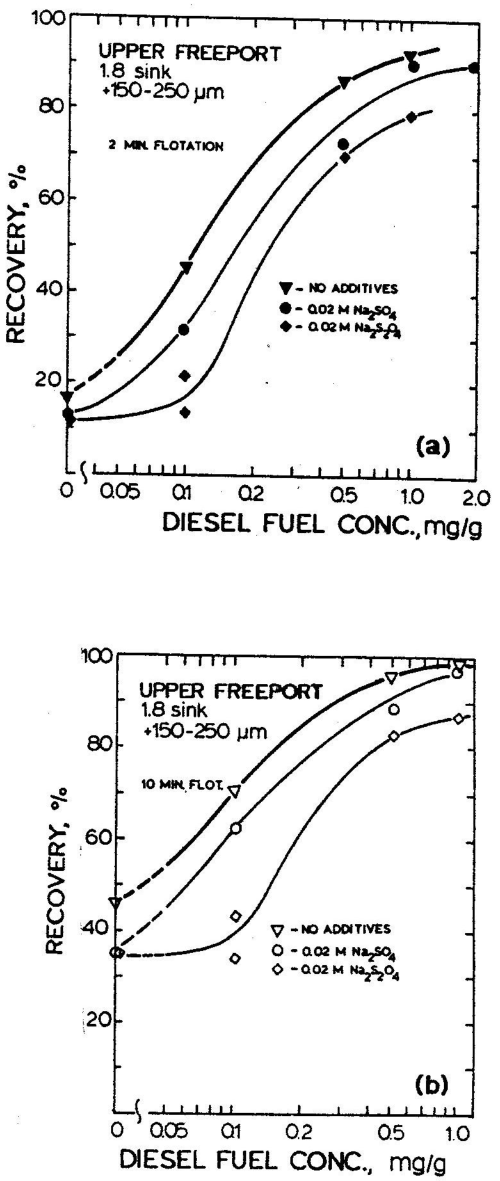

Fig. 6.
Recovery - diesel fuel concentration plot for Upper Freeport 1.80 sink fraction after 2 minutes (a) and 10 minutes (b) of flotation.

was not successful as it was observed for Lower Kittanning coal. However, the microflotation experiments performed in the presence of sodium dithionite indicated the possibility of enhanced selectivity of separation due to observed significant depression of 1.80 sink fraction and an improvement in flotation of 1.40 float fraction, when the additive was present in the flotation slurry.

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STRESZCZENIE

Chmielewski T., Birlingmair D.H., Pollard J.L, 1991, Wpływ dwutionianu sodowego na flotację pirytu i węgla za pomocą oleju napędowego. Fizykochemiczne Problemy Mineralurgii, 23, 115-125.

Badano wpływ czynnika redukującego -dwutionianu sodowego $(Na_2S_2O_4)$ - na mikroflotację pirytu i dwu amerykańskich węgli (Lower Kittanning i Upper Freeport) o różnej hydrofobowości. Wykazano, że w obecności dwutionianu sodowego następuje znaczne obniżenie flotowalności bezkolektorowej i flotowalności przy użyciu oleju napędowego dla hydrofobowego, siarkowanego pirytu. Stwierdzono również obniżenie flotowalności w obecności kolektora olejowego dla świeżo zmielonego, niesiarkowanego pirytu. Testy flotacyjne wykonane dla dwóch różnych frakcji (1.40 float i 1.80 sink) wykazały, że w obecności dwutionianu następuje wzrost flotowalności frakcji organicznej i obniżenie flotowalności frakcji mineralnej węgla Upper Freeport. Podobne testy wykonane dla dwu frakcji węla Lower Kittanning nie potwierdziły wpływu czynnika redukującego na flotowalność.