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RECOVERY OF FOSSIL RESIN FROM COAL FINES

Processing technology for fossil resin recovery from the Wasatch Plateau coal deposits (Utah, USA) is described. It was found during traditional materials handling of the run-of-mine coal that the fossil resin tends to concentrate in coal fines fraction. The influence of frother type, pulp concentration and pH on concentrate grade and recovery was examined during flotation of $< 650 \mu\text{m}$ (–28 mesh) and $< 150 \mu\text{m}$ (–100 mesh) coal fractions. The resin was extracted from the wet flotation concentrate using a heptane-in-water emulsion. The extraction rate and resin recovery were improved when the emulsion was stabilized with surfactants. The surfactant type (anionic, cationic and nonionic) had minimal influence on the extraction performance.

COAL FOSSIL RESIN OCCURRENCE AND PROPERTIES

Many bituminous coals around the world contain considerable quantities of coal-derived fossil resin. Some seams of the Wasatch Plateau coal field in Utah, USA, contain as much as 5% resin (Miller and Ye 1989). Because macroscopic fossil resin is friable, it tends to concentrate into the fines during coal handling, and the $< 650 \mu\text{m}$ (–28 mesh) coal stream in coal preparation plant can contain more than 10% resin.

The chemical nature of resin is rather complex but thermogravimetric and spectrometric analyzes suggest that the fossil resins from the Wasatch Plateau contain mainly polymerized sesquiterpenoids (Crelling et al. 1987), see Fig. 1. All terpenoids contain some level of unsaturated carbon bonds and carbonyl or carboxylic groups, but the aromaticity of the Wasatch Plateau resin is rather low, only 0.06 as determined by NMR (Yu et al. 1991).

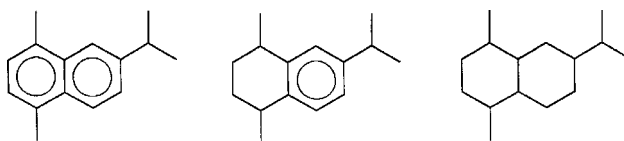


Fig.1. Sesquiterpenes present in the Wasatch Plateau resin

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Macroscopic fossil resin is a friable solid with colors changing from yellow to dark brown and a melting point in the range of 140–178 °C. The density of resin is about 1.036 g/cm³. The solubility of resin in aromatic and aliphatic hydrocarbon solvents is excellent (Yu et al. 1992).

Due to unique physicochemical properties, fossil resin can compete in the market with synthetic resin and is a desirable resource for use in many different chemical industries. The main market is the printing ink industry, where fossil resin is a valued additive especially in offset ink compositions, and has particular advantage in high speed printing technologies. Other possibilities of resin utilization are adhesives, rubber, paint, coatings and thermoplastic industries (Irwin 1990).

Fossil resin has been recovered on a small scale from the Wasatch Plateau coal field since 1929 by gravity or flotation. Commercial technology has not yet been developed and the valuable resin is being burned for electric power generation. Purified resin has a market value of \$2 per kg. Assuming only 2% recoverable resin content in coal, the Wasatch Plateau coal field is worth more for its resin content than for its fuel value.

In this regard, the possibilities of fossil resin recovery have been intensely investigated in the last two decades and several new flotation techniques were developed (Laros and Pick 1983, Arabidze et al. 1980, Miller and Ye 1988, Miller et al. 1990, Miller et al. 1992). The flotation concentrates contain about 60% resin and have to be refined by solvent extraction. The market value of the refined resin depends up on its color. Light colored resin has a higher market value than dark resin. The color shade depends on the solvent type and extraction conditions (Yu et al. 1991). The most appropriate solvents are aliphatic hydrocarbons. Until recently the flotation concentrate containing at least 25% water, was dried prior solvent extraction. In the present paper fossil resin was beneficiated by flotation and the wet concentrate was refined by solvent extraction without drying.

ANALYSIS OF FINE COAL FEED

In this study < 650 μm (–28 mesh) and < 150 μm (–100 mesh) coal fines, obtained from the Cyprus Plateau Coal Preparation Plant, were used as the source of resin. After pulverization each coal sample was analyzed for resin content (heptane soluble by Soxhlet extraction) and ash content. The results are compared in Table 1 with the composition of the < 15 cm (–6 inch) run-of-mine coal.

The data in Table 1 confirm previous observations that finer coal size fractions contain more fossil resin and only slightly more ash. The concentration ratio for resin, compared to the < 15 cm (–6 inch) coal, equals 3 for the < 650 μm (–28 mesh) fines, and almost 4.5 for the < 150 μm (–100 mesh) slimes.

Table 1. Results of feed analysis

Coal Sample	Content [% wt]	
	Resin	Ash
15 cm (6 inch)	2.27	19.81
650 μm (28 mesh)	7.19	20.49
150 μm (100 mesh)	10.04	25.34

FLOTATION OF RESIN

The fossil resin was separated from the < 650 μm (–28 mesh) and < 150 μm (–100 mesh) coal fines by conventional flotation in a 2-liter cell using a Denver-type flotation machine. The same flotation conditions were used in all experiments:

- pH was controlled by $\text{Ca}(\text{OH})_2$ addition (up to 2 kg/ton),
- 2 min conditioning time after lime addition,
- 7 min flotation time,
- rotor speed 950 rpm,
- air flow rate 4 dm^3/min ,
- flotation temperature 20 $^\circ\text{C}$,
- no collector.

The flotation efficiency was evaluated in terms of the concentrate grade, the resin recovery to the concentrate, and the flotation yield. Methyl *iso*-butylcarbinol (MIBC), Aldrich Chemical Company Inc., *iso*-amyl alcohol (AAI), Mallinckrodt Chemical Works, and three commercial frothers were examined. The influence of pulp pH, pulp concentration and frother type on the resin recovery and the resin content in the concentrate are presented in Figs. 2–7.

The data in Figs. 2 and 3 reveal that the pulp pH clearly influences the flotation performance. The concentrate grade increased twice when the pH was raised from 9.5 to 11.5. However, the resin recovery drops insignificantly. At lower pH the hydrophobicity of resin and coal particles does not differ, therefore, both resin and coal particles float together. In a more alkaline environment coal particles become more hydrophilic and remain in the slurry, while resin particles retain a high level of hydrophobicity and report to the concentrate.

Considering the impact of the solids content in the flotation cell, the process efficiency decreases in some degree when pulp density exceeds 10% by weight, regardless of the size fraction, see Figs. 4 and 5.

The influence of frother dosage on the concentrate grade and on the resin recovery is shown in Figs. 6 and 7. For increased frother addition the flotation selectivity decreased and the resin content in the concentrate was reduced, which might be

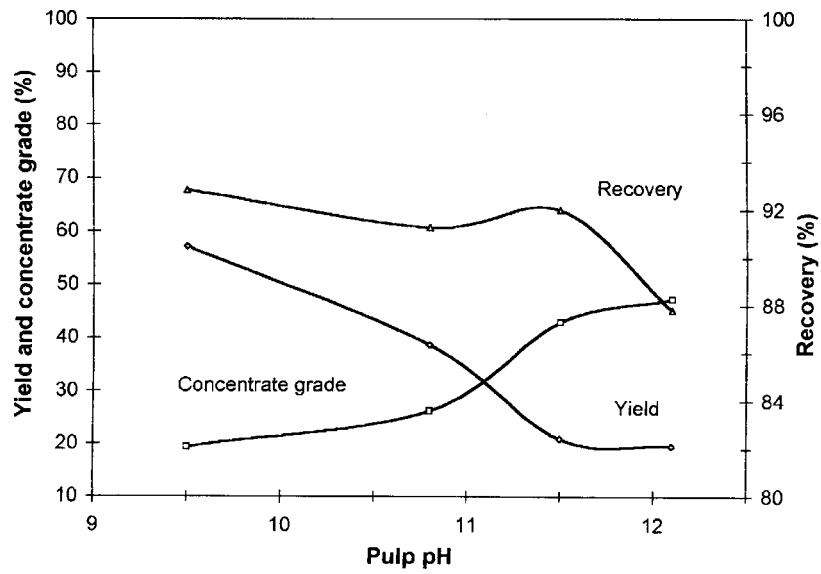


Fig. 2. Flotation results vs. pulp pH. Feed < 150 μm (-100 mesh), pulp concentration 10%, MIBC 450 g/t, flotation time 7 min

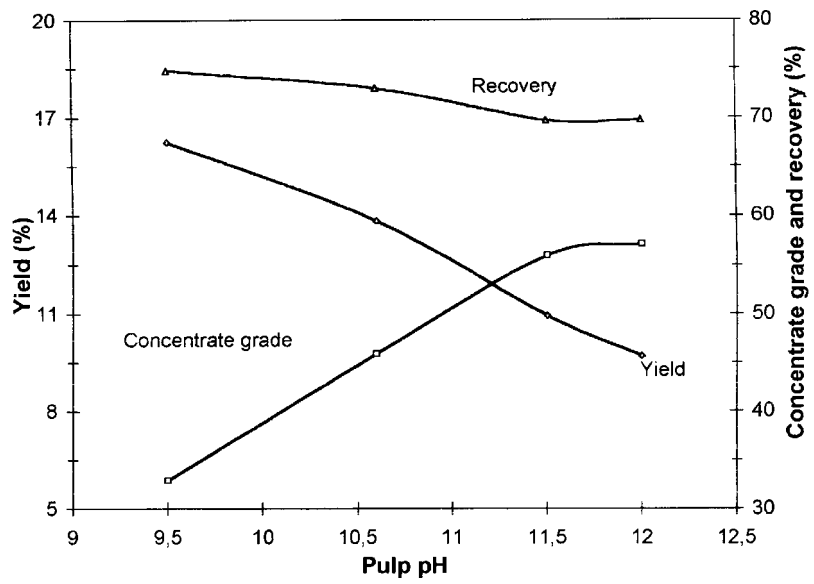


Fig. 3. Flotation results vs. pulp pH. Feed < 650 μm (-28 mesh), pulp concentration 15%, MIBC 450 g/t, flotation time 7 min

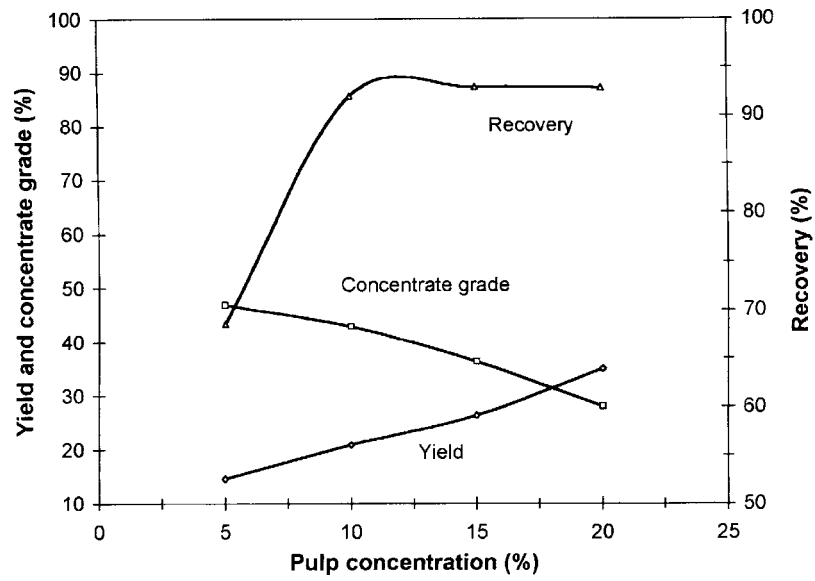


Fig. 4. Flotation results vs. pulp concentration. Feed <math>< 150 \mu\text{m}</math> (-100 mesh), pulp pH 11.5, MIBC 450 g/t, flotation time 7 min

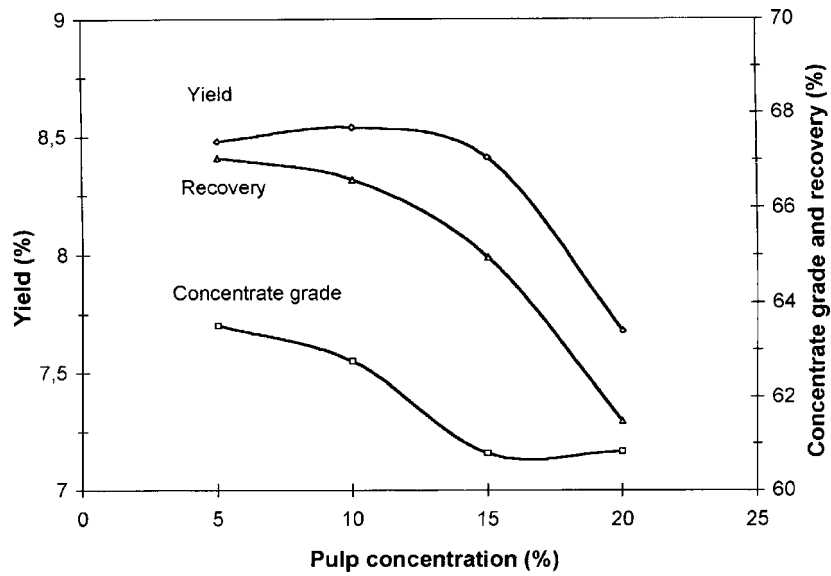


Fig. 5. Flotation results vs. pulp concentration. Feed <math>< 650 \mu\text{m}</math> (-28 mesh), pulp pH 11.7, MIBC 500 g/t, flotation time 7 min

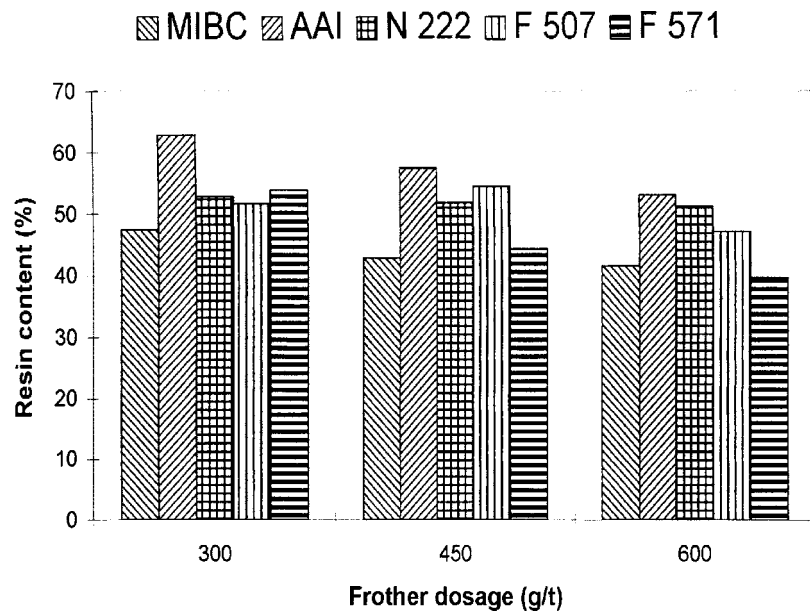


Fig. 6. The resin content of resin concentrate vs. frother type.
Feed < 150 μm (-100 mesh), pulp pH 11.7, pulp conc. 10%, flotation time 7 min

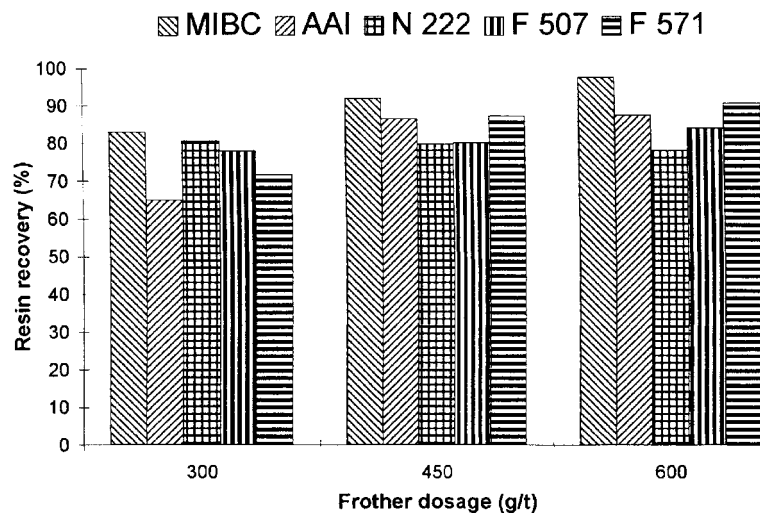


Fig. 7. The resin recovery from resin concentrate vs. frother type.
Feed < 150 μm (-100 mesh), pulp pH 11.7, pulp conc. 10%, flotation time 7 min

caused by increased frother adsorption on the coal particles. For each level of frother concentration the AAI showed the best performance. The resin recovery increased

with increasing frother dosage due to froth stabilization and because of perhaps frother adsorption on coal and resin particles. The best recovery was obtained when MIBC was used as the frother, for both minus 28 and minus 100 mesh samples.

SOLVENT EXTRACTION

The resin concentrate derived from the $< 150 \mu\text{m}$ (-100 mesh) sample, with MIBC as the frother, was used for solvent extraction experiments. The fresh concentrate was dewatered by filtration and analyzed for heptane-soluble resin and for residual water. The composition of the concentrate was 49% resin, 26% water, and 25% coal with ash. Batch extraction of wet resin concentrate was examined using a 1:1 by volume heptane-in-water emulsion. Three types of surfactants at a concentration of 40 mg/dm^3 were used to stabilize the emulsion:

- dodecylamine hydrochloride (DAC), Aldrich Chemical Company, Inc.,
- lauryl sulfate, sodium salt (SDS), Aldrich Chemical Company, Inc.,
- fatty alcohol $\text{C}_9\text{--C}_{11}$ oxyethylenated – 6 $\text{C}_2\text{H}_5\text{O}$ groups, (Rhodasurf 91–6), Rhone-Poulenc.

The emulsions were prepared in an UltraTurrax type homogenizer and immediately added to a 30% by weight aqueous suspension of resin concentrate. The extraction was carried out at 20°C in a 2 dm^3 vessel equipped with stirrer. Stirrer revolutions were maintained constant at 300 rpm. Gentle stirring is crucial to prevent formation of stubborn multiple emulsions in the system. The slurry/emulsion volumetric ratio was 1:5. During extraction 12 ml samples were withdrawn for centrifugation and the resin content of the organic phase was determined after heptane evaporation. The kinetic results of the extraction experiments are presented in Fig. 8 as the percent of recoverable resin extracted from the concentrate.

The data in Fig. 8 makes it evident that the kinetics of extraction and the resin recovery were improved when surfactants were used to stabilize the heptane-in-water emulsion. Stabilization of the emulsion apparently prevented coalescence of small droplets which resulted in more effective collisions, and finally secured a greater dissolution rate for the resin particles. Hardly any influence of the surfactant type on the process efficiency was noted. The cationic surfactant – dodecylamine hydrochloride – caused the least improvement, while the nonionic surfactant – Rhodasurf – the best. Both resin and coal particles have a negative zeta potential over a wide range of pH values. Also heptane droplets exhibit a negative zeta potential and are hydrophobic similar to the solid particles. Thus physicochemical similarities of these three surfaces suggest similar adsorption potential for each surfactants. The presence of ionic surfactants at heptane and resin surfaces may lead to increased electrostatic repulsion between the particles and hinder extraction. The nonionic surfactant would not directly influence the surface charge at the particles and did not retard the resin particle–heptane droplet coalescence.

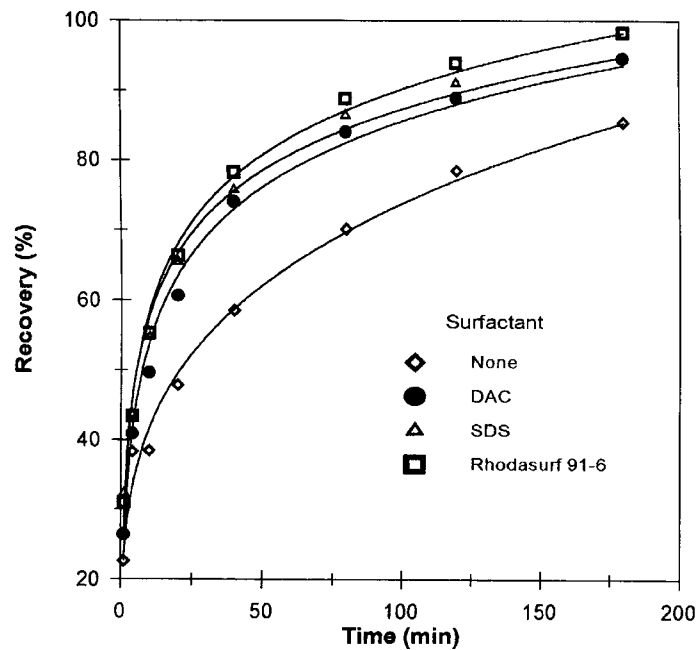


Fig. 8. Kinetics of heptane/water resin extraction without and in the presence of surfactants

CONCLUSIONS

- During traditional materials handling of the run-of-mine coal finer coal size fractions contain more fossil resin than coarser ones. Efficient flotation can be expected for fossil resin recovery from coal fines when an appropriate frother is used under alkaline conditions.

- The kinetics of resin extraction with a heptane-in-water emulsion was improved when the emulsion was stabilized with surfactants. The surfactant type (cationic, anionic, nonionic) had a much smaller impact on the extraction efficiency than might be expected. The resin recovery reached almost 100% after 3 hours of extraction in the laboratory system using the nonionic Rhodasurf 91-6 surfactant as an emulsifier.

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Miller J.D., Hupka J., Halbe D., Nalaskowski J., Liu N., Odzysk żywicy kopalnej ze szlamów węglowych. *Fizykochemiczne Problemy Mineralurgii*, 31, 211–219 (w jęz. angielskim)

W pracy przedstawiono możliwość odzysku kopalnej żywicy z węgla ze złóż Wasatch Plateau, Utah, USA. Stwierdzono, że żywica ulega koncentracji w odpadowej, drobnoziarnistej frakcji węgla. Przeprowadzono próby flotacji frakcji węgla o wymiarach ziaren $< 650 \mu\text{m}$ (-28 mesh) i $< 150 \mu\text{m}$ (-100 mesh). Zbadano wpływ rodzaju speniacza, stężenia substancji stałej i pH na stopień odzysku i zawartość żywicy w koncentracie flotacyjnym. Stwierdzono najlepszy odzysk przy użyciu metylo *iso*-butylocarbinolu (MIBC) jako speniacza, natomiast największe stężenie żywicy w koncentracie dla alkoholu *iso*-amyłowego (AAI) jako speniacza.

Przeprowadzono próby ekstrakcji żywicy z wilgotnego koncentratu przy użyciu emulsji heptan/woda. Wyznaczono kinetykę ekstrakcji. Stwierdzono dodatni wpływ stabilizacji emulsji przez surfaktanty na szybkość ekstrakcji i stopień odzysku żywicy z koncentratu. Zbadano wpływ surfaktantów: anionowego, kationowego i niejonowego, i stwierdzono minimalny wpływ rodzaju surfaktantu na proces ekstrakcji.