

THE USE OF AQUEOUS BORON TRIFLOURIDE IN DEASHING ORGANIC RICH ROCKS AND SEDIMENTS.

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Introduction.

The study of the organic matter in coal and other organic-rich rocks such as oil shale and petroleum source rocks often requires the isolation of the organic matter. The common approach is to macerate the inorganic fraction of the rock by attack with HF. This unique reagent reacts with the silicates to form SiF_4 , a volatile gas, and leaves the organic matter largely unaltered.

Unfortunately HF also reacts with other inorganic components to form fluoride salts, the most pernicious being CaF_2 , which is very insoluble. Thus HF is usually used in combination with HCl, which is used first as a pretreatment step to remove calcium carbonates, and then in combination with HF solutions in the final deashing step to prevent additional fluoride formation.

The use of HCl is undesirable, however, as it is a stronger acid than HF and has a stronger affect on the organic matter.¹ (See also Robinson and Saxby for further discussion on the affects of reagents on organic matter).^{2,3} Also chlorination reactions are possible and undesirable. The HCl is not needed to dissolve carbonates as the HF is normally used in sufficiently high concentration to dissolve them.

The approach taken in this work is to selectively dissolve neo-formed fluorides in a two step demineralizing process, by reaction with BF_3 , which is a highly water soluble gas. The BF_3 is generated by the reaction of H_3BO_3 with HF,



and it then reacts with neo-formed fluoride salts, such as fluorite, to form water soluble fluoroborates.

Methods.

Samples and Sample Preparation. Four oil shales including the Stuart from Australia, the Green River from the U.S. (Rock Springs, Wyoming), the Irati from Brazil (Sao Mateus do Sul) and a sample of the Israeli Rotem (or E'fe) oil shale were used as test materials. The Stuart and Irati are silicates and the Israeli and Green River are carbonate shales. Two coal

samples, obtained from the Argonne National Laboratory (ANL) premium sample bank, were used in the experiments; these are the North Dakota lignite (Beulah-Zap Seam) and the Wyoming subbituminous coal (Wyodak-Anderson Seam).⁴

The oil shale was crushed to approximately -1/4" in a jaw crusher. The -100 mesh material was sieved out and the remainder of the sample passed through a Rieche mill equipped with a 100 mesh screen. The samples were then re-homogenized. The samples of lignite and subbituminous coal from ANL were used as received (-100 mesh).

HF-HCl Demineralization Procedure. For comparison purpose a fraction of the test samples were processed using a typical HCl-HF procedure.¹ Approximately 20 g of sample was stirred for 24 hours at room temperature in a sealed 1 liter heavy duty centrifuge bottle filled with 6 N HCl. The sample was then centrifuged and the residual acid decanted off through 0.45 micron filters. Material trapped on the filters was washed back into the sample containers. The sample was washed by completely resuspending it in distilled-deionized water and centrifuging. Approximately 900 ml of a 1:1 (v/v) solution of 6 N HCl and 48% HF mixture was then added to the sample, which was capped and left at room temperature overnight on a magnetic stirrer. The sample was then centrifuged and washed 5 to 6 times with distilled-deionized water, decanting each time through a 0.45 micron filter and rinsing the filtrate back to the sample. The sample was dried in a vacuum oven at 60°C overnight and disaggregated by crushing with a mortar and pestle.

Boron Trifluoride Procedure. Twenty g of sample was placed in heavy duty 1 liter centrifuge bottles and 800 ml of 1:1 v/v 48% reagent grade HF added. For samples which contained carbonates, the acid was initially added in 10 ml increments to prevent spillage from excessive foaming due to the generation of CO₂. The foaming generally ceased after approximately 40 to 50 ml of HF was added. The sample was sealed, left at room temperature and stirred overnight on magnetic stir plate. The following morning the sample was chilled in an ice bath and 250 g of boric acid was added in two 125 g increments with time left between additions for the sample to recool. The reaction of H₃BO₃ with HF is exothermic and the sample was pre-cooled to 0°C to minimize the loss of BF₃. The sample was again tightly capped and left at room temperature to stir overnight. The following day the sample was centrifuged, the supernate poured through a 0.45 micron filter and washed back to the sample. The sample was each washed 5 to 6 time by completely resuspending it in distilled-deionized water and centrifuging. It was then dried in a vacuum oven at 60°C overnight.

Discussion.

The demineralized samples are composed of concentrated organic matter and residual ash which, for the most part, consist of sulfides (pyrite and marcasite). Based upon previous experience rutile and zircon are also expected to be present.⁵ The total ash in the test samples varied from ~0.1% in the Wyoming subbituminous and North Dakota lignite samples to ~29% in the Irati oil shale samples. A comparison of the residual ash for sample processed by the two techniques indicate no substantive differences, with the HF-BF₃ technique producing slightly lower ash (Table 1).

Based upon the comparison of FTIR spectra, the organic matter in the samples processed with the HF-BF₃ technique does not appear to be altered more than that processed by the HF-HCl technique. Although additional analysis is needed, the currently level of data suggests that the HF-BF₃ procedure actual results in less organic mater alteration than the

HF-HCL procedure.

The mechanism of the BF_3 -fluoride salt reaction is of interest. A search of the literature and consideration of the stoichiometry involve indicated that two reactions are possible,^{6,7}



or



Model compound studies employing optical grade crystalline CaF_2 and $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ were used to explore the possible reactions. The dissolution of CaF_2 was found to depend directly upon the BF_3 concentration (Figure 1) with an equilibrium constant of 0.12. Thus, reaction 2, the formation of calcium fluoride tetrafluoroborate, is indicated. During the dissolution experiments, a tan color precipitate was found to begin forming at the point where the calculated concentration of $\text{CaF}(\text{BF}_4)$ is ~ 36 g/l, which we believe to be the approximate solubility of this salt.

In summary, the HF- BF_3 technique has certain advantageous over the more traditional approach employing HCl. Because all of the HF is converted to fluoroborates the need to handle large quantities of contaminated HF is eliminated. This approach also results in samples with as low or lower residual ash and does not alter the organic matter any more, and probably less than, more traditional techniques employing HCl.

References.

1. Durand, B. and G. Nicaise, Ch. 2, In, *Kerogen, Insoluble Organic Matter from Sedimentary Rocks*, B. Durand (Ed.), Editions Technip, Paris, p. 36, 1980.
2. Robinson, W.E., Ch. 6, In, *Organic Geochemistry*, G. Eglinton and M.T.J. Murphy (Eds.), Springer Verlag, New York, 1976.
3. Saxby, J.D., In *Oil Shale*, Yen, T.F. and G.V. Chilingarian (Eds), Elsevier, p. 104, 1976.
4. Vorres, K.S., 1991, *Energy and Fuels*, 4, p. 420-426.
5. Robl, T.L., D.N. Taulbee, L.S. Barron and W.C. Jones, 1987, *Energy and Fuels*, 1, p. 507-513.
6. Paevlenko, S., *Z. anorg. allg. Chemie.*, 301, p. 337, 1959.
7. Paevlenko, S., *Z. anorg. allg. Chemie*, 315, p. 136, 1962.

Table 1. Comparison of Residual Ash from Demineralization of Coals and Oil Shales with HF-HCl and HF-BF₃ Procedures.

Demineralizing Procedure	HF-HCl	HF-BF ₃
Oil Shales	%Ash	%Ash
Irati Oil Shale-Upper Bench	29.3	26.3
Israeli Oil Shale-E'fe	7.1	6.7
Green River Shale-Tipton Member	9.6	8.8
Stuart-Kerosene Creek Member	9.7	7.2
Coals		
Wyoming Subbituminous-Wyodak	<0.1	<0.1
North Dakota Lignite-Beulah Zap	<0.1	<0.1

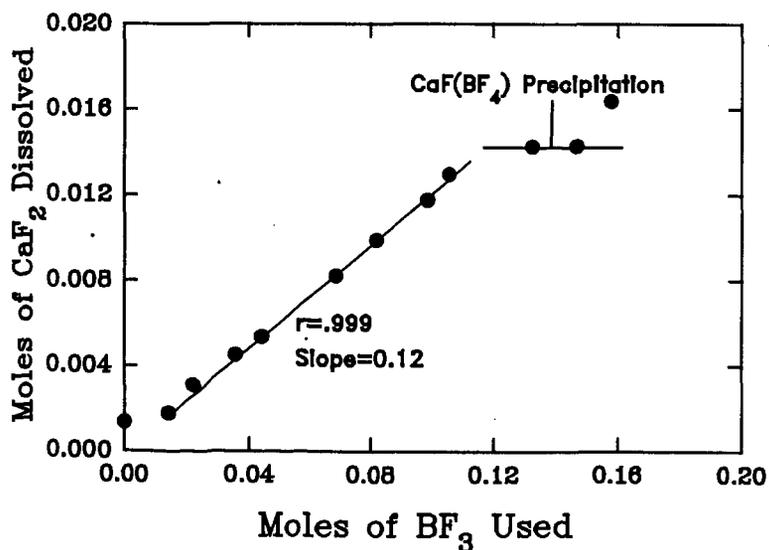


Figure 1. Plot of CaF₂ dissolved versus BF₃ added in modal compound study.