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A brief hydrologic and geologic reconnaissance in the Cordova area, Alaska

By Ivan Barnes

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The lower reaches of streams from Cordova, Alaska, east to the Bering River, show a variety of habitats. White turbid reaches, presumably due to glacial flour, tan to brown-colored reaches, presumably colored by tannins, orange to rust-colored turbid reaches, laden with ferric hydroxide ($Fe(OH)3$) and clear reaches were observed. The white turbid reaches flow immediately from glacial melting. Tan to brown-colored reaches are from fermenting organic material buried in the alluvium of the outwash plains. Some of this organic material may bring iron into solution in the water in the form of chemical combinations or complexes with the organic molecules. Orange to rust-colored turbid reaches are due to the oxidation of ferrous ion and the hydrolytic precipitation of ferric hydroxide ($Fe(OH)_3$). Reactions of ferrous iron with atmospheric oxygen dissolved in the river water may be represented as

$$O_2 + 4Fe^{+2} + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$$

The total reaction will occur without the intervention of organic processes. If it is promoted by biological means, for instance, bacteria, the reaction will be faster but produces the same result, and if much dissolved ferrous iron is available the stream bed may be covered with a deposit of red or orange $Fe(OH)_3$. The glacial flour-laden streams and the clear reaches are beyond the scope of this report but the reactions in organic-rich sediments are a guide to what may be expected if coal is mined in the area. Plant material, upon burial within sediments or submergence beneath water, may break down rapidly at first with the leaching of more soluble components. Doubtless such leaching gives rise to the organically colored water. Iron may be present in the colored water in the form of organic complexes. The iron is only slowly released from organic complexes because there must first be some reaction to release the iron from the complex. The complex commonly is oxidized as in the reaction

$$\text{complex Fe} + O_2 \rightarrow CO_2 + H_2O + \text{organic residue} + Fe^{+3}.$$

The slow reactions of complexed iron result in a dispersal of iron precipitates over larger areas of the stream bed.

Organic material continues to ferment in underwater environments, after leaching of readily soluble organic materials. With sluggish circulation or in the presence of abundant organic material, oxygen is depleted as the organic material is altered. The oxygen removal is an oxidizing reaction (consumes electrons) and is coupled with organic reactions such as

alcohols	to	aldehydes
RCH_2OH	$\rightarrow$	$RCHO + 2H^+ \; 2e^-$
aldehydes	to	acids
$H_2O + RCHO$	$\rightarrow$	$RCOOH + 2H^+ + 2e^-$

acids to carbon dioxide + organic residue

$$RCOOH \rightarrow CO_2 + 2H^+ + 2e^- + R$$

(where R represents organic structures consisting mainly of carbon and hydrogen)

Although written schematically as a string of chemical reactions, the reactions in detail are quite complex and had best be described as fermentation by biologic agencies. No matter how described, the loss of dissolved oxygen results in an increase in the solubility of iron as the always present oxides and hydroxides of ferric iron react in the reducing (oxygen-poor) environment to produce ferrous ions:.

$$2e^- + Fe_2O_3 + 6H^+ \rightarrow 2Fe^{+2} + 3H_2O$$

$$\text{and} \quad e^- + Fe(OH)_3 + 3H^+ \rightarrow Fe^{+2} + 3H_2O \, .$$

Note that the solubility of iron minerals is controlled by reduction rather than acidity. As the iron-bearing water discharges through stream beds and comes in contact with O_2-containing stream water, a favorable environment for iron-oxidizing organisms is created. The organisms use the chemical energy from the reactions between ferrous iron and oxygen for their life processes. Unfortunately, Fe^{+3} (ferric ion) is insoluble at pH levels above 4. The reaction between ferric ions and water

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

tends to lower the pH and foul the bed with $Fe(OH)_3$. In the Cordova, Alaska area, the copious supply of water may dilute the H^+ so a toxically acid condition may not materialize if enough dilution and flushing occur, but the fouling of stream beds with $Fe(OH)_3$ may still be an adverse effect.

Addition of more organic material, including coal, to the hydrologic environment can only aggravate the iron fouling condition now found. Coal is not inert. A spring issuing from the coal exposed by trenching in the Carbon Creek drainage (SW¼sec. 15, T. 17S., R. 7E.) has a pH of 9.5 and a pronounced H_2S odor. From the distribution of $Fe(OH)_3$ staining above the coal the reactions apparently involve oxidation of pyrite which may occur in the presence of dissolved oxygen.

$$14H_2O + 15\ O_2 + 4FeS_2 \rightarrow 8SO_4^{-2} + 4Fe(OH)_3 + 16H^+$$

The SO_4^{-2} remains in solution and by bacterial oxidation of the coal yields

$$2H^+ + SO_4^{-2} + 2C\ (\text{coal}) \rightarrow 2CO_2 + H_2S\ .$$

Because this process consumes H^+ there is a pH rise from the 6.8 to 6.9, reported from springs in the area to the pH of 9.5 measured in the H_2S rich spring. Interestingly, a rich growth of colorless filamentous organisms, probably sulfur oxidizing bacteria, are found in the channel occupied by the H_2S containing water from the spring.

In summary, addition of coal to the sediments of the river systems near Cordova may be expected to increase the bottom fouling conditions. A comparative biologic study of the $Fe(OH)_3$ fouled reaches, the organic colored reaches and the clear water reaches should reveal adverse biologic consequences. Toxic pH levels may be found if insufficient dilution or large enough Fe^{+2} oxidation rates occur.

Not all of the trenching at and near the coal seam was visible due to the snow cover. Detailed examination of the accessible exploration workings revealed that the coal is regionally conformable with the shale exposed with a strike of N. and a dip of 55^{o} to the west. The land surface slopes 25^{o} to the west. For every foot west from the outcrop the land surface decreases .47 ft. The coal dips 1.43 ft. for every horizontal foot to the west and the difference, 0.96, represents the increase in overburden in feet <u>per foot</u> horizontally normal to the strike. For example, 96 feet of overburden will have to be removed to mine the coal 100 ft. horizontally west of the outcrop.

It should be mentioned that the topography is rugged. There does not seem to be a storage area for overburden that will prevent severe erosion loss of the overburden. The erosion of overburden will increase the sediment load of receiving streams. If the stream sediment-carrying capacity is exceeded, sediment deposition in the drainage is to be expected.

As mentioned above, the coal has the regional attitude. Shale and graywacke along Charlotte Ridge strikes N. 10^{o}E. and dips 45^{o}W. in good agreement with the coal-shale contact. In detail the coal is folded into the shale in part and is quite friable in outcrop. Coal lumps may be crushed between the fingers to roughly equant fragments of 1 mm. or less on an edge. The fractures are on three orthogonal joint sets including an axial plane cleavage in smaller folds. It would be impracticable to remove such coal without losing coal to the streams in the drainage. A qualitative experiment was made. Turbid (black) water from a stream draining the trenching operation was sampled after one man forded the stream. Two days standing failed to settle the black turbidity from the 500 ml sample. Flocculation treatment would be advisable to prevent loss of fines to the drainage during and following mining until protective cover could be reestablished.

This concludes the report undertaken for the U.S. Forest Service. We wish to thank the U.S.F.S. personnel for their invaluable support and help during the field study conducted during the period June 26-29, 1970. Kenneth Mitchell and Ray Clark were especially helpful and have our deepest thanks. If there are further questions we would be glad to answer them to the extent of our abilities.