

HUMIC ACIDS FROM LEONARDITE -- A SOIL CONDITIONER
AND ORGANIC FERTILIZER

Roger W. Youngs and Clyde M. Frost

U. S. Department of the Interior, Grand Forks
Lignite Research Laboratory, Bureau of Mines,
Grand Forks, N. Dak.

The term "humic acid" was first applied in 1826 by Sprengel (9) to that brown amorphous precipitate which is obtained by acidifying the alkali extract of decayed organic matter in soil. Since the inception of the term, humic acids have been extracted not only from soil but also from peat, brown coal, oxidized bituminous coal, and even from artificial materials obtained in the laboratory by action of inorganic acids or oxidizing agents on carbohydrates, proteins, and phenols. Odin (8) in 1922 redefined humic acids as yellow-brown to black-brown substances of unknown constitution, formed in nature by decomposition of organic materials under atmospheric influence or in the laboratory by chemical action. Humic acids can split off hydrogen ions and form typical salts with strong bases and usually are insoluble in water, soluble in alkali, and reprecipitated by acid. In general, humic acids are not chemically uniform substances, but are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000 units. Their micelles carry a negative charge. The alkali solubility of humic acid is due to carboxyl and phenolic hydroxyl groups which account for about 22 percent of the weight of the molecule.

Humic acid is an essential part of soil. It is this material, present in good soil, that fixes nitrogen, makes available to the plant, through base exchange, the soil nutrients, and improves the physical structure of the soil. In recent years, much research has been conducted, particularly in India, Japan, Germany, Russia, and France, on replenishing the depleted humic acids of soils with the so-called "regenerated humic acids" obtained by oxidation of coal. These regenerated acids, which closely resemble the natural humic acids, have either been added directly to the soil or first supplemented with plant nutrients. Greenhouse and field tests have shown that these humic acid preparations improve plant yields (3), decrease loss of moisture from the soil (6), and increase the workability of the soil (2).

As a convenient and commercial source of humic acids, extensive reserves of naturally-oxidized lignite occur with virtually all lignite outcrops in North Dakota. This naturally-oxidized material, which contains up to 86 percent humic acids on a moisture-and-ash-free basis, has been given the name "leonardite," after A. G. Leonard, first director of the North Dakota Geological Survey, who did much of the early studies on these deposits (1). Leonardite is a coallike substance similar in structure to lignite, but significantly different in its oxygen and ash contents. In Table 1 the ultimate analyses of lignite, leonardite, lignite oxidized with air in the laboratory at 150° C, and humic acid extracted from leonardite with 1N NaOH are compared. The ash content of leonardite varies from mine to mine but is usually between 15 and 30 percent on a moisture-free basis.

TABLE 1. - Analyses of lignitic materials, percent

	Leonardite	Lignite	Oxidized lignite	Humic acid extracted from leonardite by 1N NaOH
Ash (mf)	18.7	10.0	10.7	3.9
Hydrogen (maf)	4.0	5.1	2.9	3.4
Carbon (maf)	65.2	72.8	65.4	63.5
Nitrogen (maf)	1.3	1.2	1.4	1.3
Oxygen (maf)	26.6	19.9	29.2	31.1
Sulfur (maf)	2.9	1.0	1.1	0.7

AMMONIATION OF LEONARDITE

Nitrogen-enriched coal humic fertilizers have received much emphasis in the past few years. Recent investigations have indicated that these products perform well as conventional fertilizers and release nitrogen more slowly. The main problem in technology is to develop a product with sufficiently-high nitrogen content (around 20 pct) which will still remain commercially competitive.

To determine if leonardite could be ammoniated to a product containing sufficient nitrogen for use as an organic fertilizer, samples were prepared by three different methods: (1) Ammoniation in an aqueous slurry, (2) ammoniation in an upward moving gas stream through a column of dried leonardite, and (3) ammoniation under pressure of 2,000 psig at 200° C. The nitrogen analyses of these variously ammoniated leonardite samples and the analysis of an aqueously ammoniated humic acid extracted from leonardite appear in table 2. The increase of nitrogen content of leonardite, even under radical conditions, is not sufficient for it to be used as an organic fertilizer. The nitrogen content of the ammoniated humic acid increased 2.5 times over that of the correspondingly ammoniated leonardite sample. The higher ash content, as well as the 15-percent nonhumic carbonaceous material in the leonardite, accounts for the decreased reactivity with ammonia. Therefore, to prepare a high-nitrogen organic fertilizer, the humic acids would first have to be extracted from the leonardite.

TABLE 2. - Nitrogen analyses of variously ammoniated samples, percent
(Moisture-free basis)

Sample	Method of ammoniation		
	1	2	3
Leonardite	3.87	2.82	11.15
Humic acid	8.13	-	-

RECOVERY OF HUMIC ACIDS FROM LEONARDITE

One part of the work at this laboratory was to find an inexpensive, rapid method for obtaining from leonardite bulk quantities of low-ash humic acids which could be used in preparing a soil conditioner and high-nitrogen-content organic fertilizer. The humic acids in leonardite are bound to the ash largely as insoluble calcium salts. Therefore, to recover the humic acids requires not only a physical means

of removing the clay and sand, but also a chemical treatment to displace the calcium ion. In the past, alkali extraction of the humic acids with removal of the insolubles by centrifuging the humate solution was the standard procedure for obtaining low-ash humic acids (5). The alkali extraction process, however, requires not only fresh alkali for each lot of humic acid prepared but also an equivalent amount of acid to set the humic acid free, both of which are used up in the process. The large volumes of water, which must be used to obtain a low-ash product, plus the unfilterable nature of the alkali humate solution and acid-precipitated humic acid, make the alkali extraction of humic acids unattractive. The problem of eliminating alkali extraction as the method of preparing low-ash humic acids was approached by two different routes: (1) Removing the ash physically and chemically from the leonardite, leaving a carbonaceous product containing around 85 percent humic acid, and (2) extracting the humic acid from the leonardite with an organic solvent that could be reclaimed for further extractions.

Float-Sink Process. Figure 1 schematically represents the process that was used in our experiments. Partially-dried, pulverized leonardite was added to a separatory funnel containing CCl_4 as the dense medium. The float fraction containing the humic acids was transferred to a filter, and the CCl_4 was removed. The product was washed first with a dilute H_2SO_4 solution, then with warm water. The results of this experiment appear in table 3. A ZnCl_2 solution was tried in place of CCl_4 , but absorption of the solution on the carbonaceous material caused the latter to sink, resulting in a low yield of humic material.

TABLE 3. - An examination of the float-sink process, moisture-free basis, results given in percent

<u>Feed</u> <u>Ash</u>	<u>Product</u>			<u>Tailings</u>	
	<u>Yield</u>	<u>Ash</u>	<u>Humic Acid</u>	<u>Yield</u>	<u>Ash</u>
17.7	73.1	3.5	89.0	17.4	56.8

Note - Not included in data is loss of water-soluble material.

Flotation Process. The flotation process for ash separation is schematically depicted in figure 2. The as-received, pulverized leonardite was added to the flotation cell, which contained a lignite-tar creosote fraction as a frothing agent. The froth was collected on a filter, and the filter cake was washed with dilute H_2SO_4 , followed by warm water. Results of a typical experiment in this process appear in table 4.

TABLE 4. - Analysis of the flotation process, percent

<u>Feed</u>		<u>Product</u>		
<u>Moisture</u>	<u>Ash (mf)</u>	<u>Moisture</u>	<u>Ash (mf)</u>	<u>Yield (mf)</u>
9.5	18.2	6.0	11.3	13.6

Organic-Solvent Extraction Process. The use of an organic solvent for extraction of humic acids would be most attractive if the solvent could be reclaimed by distillation and reused without reaction with or being absorbed on the humic acids. Polansky and Kinney (7) made an extensive survey of organic solvents and solvent mixtures regarding their ability to disperse humic acids from nitric acid-oxidized bituminous coal. They concluded that the most economical and most easily handled solvent for the commercial extraction of humic acids is a mixture of

acetone and water. Fowkes and Frost (4) showed that an acetone-water solution would extract humic acids from leonardite provided the leonardite was pretreated with dilute mineral acid. The amount of humic acids extractable was directly proportional to the amount of mineral acid used in the pretreatment. The several preliminary experiments conducted revealed that the most efficient extraction was accomplished using one liter of 80-20 acetone-water (percent by volume) and 10 grams of HCl (basis: hydrogen chloride) per 100 grams of leonardite (moisture-free). Ten grams of HCl per 100 grams of leonardite is slightly in excess of the acid that will be necessary to replace the calcium ion with hydrogen ions in an average leonardite sample. Sulfuric acid was tried in place of HCl as the source for the displacing H-ions, but the resulting CaSO_4 , mixed with the humic acids, resulted in an unfilterable product with a high ash content. In the first experiments, the mode of extraction was a countercurrent column. An acetone-water-HCl pretreated leonardite slurry was added to the top of the column while a solution of acetone-water was forced slowly upward through the slurry. The yields of humic acids were good, but the ash content of the product was high, indicating some carryover of ash. Later experiments showed that sedimentation of ash and nonhumic carbonaceous material in an acetone-water-HCl solution is quite rapid; thus a simple settling tank replaced the countercurrent column in the process. A flow diagram of the process appears in figure 3. The results of the experiments appear in table 5.

TABLE 5. - Analysis of the acetone-water-HCl extraction of humic acid from leonardite, moisture-free basis, percent

Feed Ash (mf)	Product			Tailings	
	Yield (mf)	ash (mf)	NaOH-soluble (mf)	Yield (mf)	Ash (mf)
17.8	64.9	1.8	96.8	31.1	38.2
			{ C 63.5		
			{ H 3.8		
	Elemental		{ N 1.0		
	(maf)		{ S 0.7		
			{ O 31.0		

Note - Not included in data is loss of water- and acid-soluble material

DISCUSSION

A comparison of the three processes investigated reveals the drawbacks of the float-sink and the flotation processes. The float-sink separation requires a non-polar medium, carbon tetrachloride, which is absorbed to some extent on the leonardite. The use of CCl_4 , plus the fact that the leonardite must be partially dried before separation, makes this process unattractive commercially. The flotation process did not produce the desired results. Owing to the low hydrophobicity of leonardite, caused by the large number of carboxyl and hydroxyl groups on the micelle's periphery, the yields of humic acids were low and their ash contents high. Attempts to precondition the leonardite with a light neutral fraction of coal tar to increase its hydrophobicity failed. Changing the frothing agents several times also gave poor results. The acetone-water-HCl extraction of humic acids lends itself most favorably to a commercial process. The yield of low-ash product is high. The acetone is easily recovered by distillation at a low temperature, and the loss is very small. Acetone does not react with, nor is it absorbed on, the humic acids. The process requires

simple equipment (a sedimentation setup works quite well), and the insolubles settle rapidly. The humic acids are easily filtered once the acetone is removed, and a minimum amount of wash water is needed to obtain a low-ash product.

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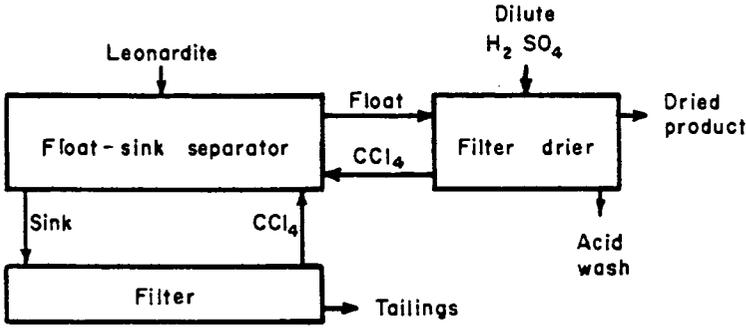


Fig. 1 Float-sink separation.

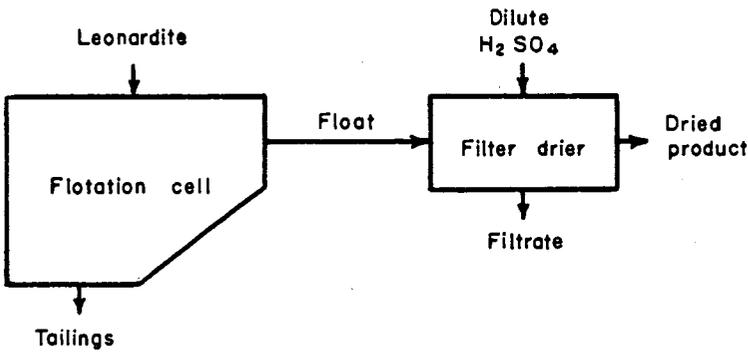


Fig. 2 Flotation process.

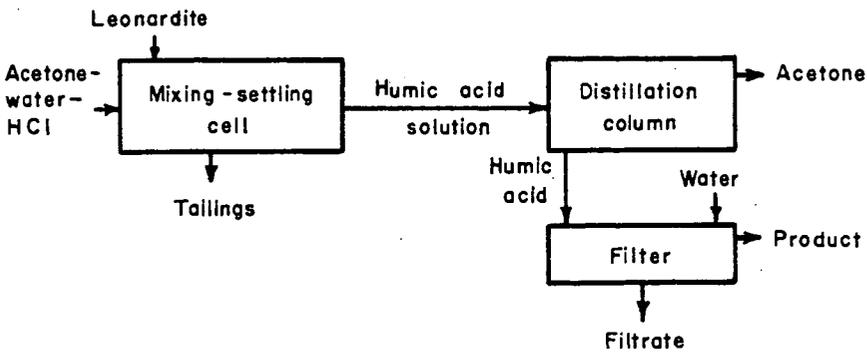


Fig. 3 Organic-solvent extraction.