

REMOVAL OF SYNTHETIC CRUDE NITROGENOUS COMPOUNDS  
USING WASTE MINERALS

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INTRODUCTION

Nitrogenous compounds in crude oils and petroleum products have been associated with several problems in processing operations and must be removed in the early stages of upgrading. With conventional technology this is done by severe hydrotreating which has several disadvantages: high capital cost investment, degradation of valuable material, and high operating cost due to energy and hydrogen consumption. A method allowing the separation of nitrogenous compounds from feedstocks would greatly reduce the costs of upgrading.

Several analytical procedures are known for the separation of nitrogenous compounds (1-7). These methods, however, are not feasible for large scale operation.

In this study waste minerals have been tested as low cost adsorbents. Since sulphide minerals are known as good adsorbents a series of sulphides was tested (5). We also tested brominated ilmenite in an attempt to take advantage of the complexing properties of titanium and iron (6,7).

EXPERIMENTAL

SULPHIDE MINERALS

The adsorption studies were conducted by liquid chromatographic methods. The feed was a solution of four or five nitrogenous model compounds dissolved in 50:50 heptane/toluene. Each compound contributed 25 ppm N to the solution. The adsorbents were natural waste minerals: pyrrhotite (FeS), pyrite (FeS<sub>2</sub>), sphalerite (ZnS), and chalcopyrite (FeCuS<sub>2</sub>).

The adsorbent (200 mesh) was dry-packed in a stainless steel column (60 cm long x 0.4 cm I.D.).

The solution of the nitrogen compounds was pumped into the column at 1 mL/min. Samples of 2 mL were collected and analyzed by gas chromatography using a Varian 6000 gas chromatograph and a Dexsil-300 packed column.

The area of the chromatographic peaks was used to calculate the percentage of each component present in the effluents. The calculations were made as follows:

$$\% \text{ Species } i = \frac{\text{area of peak } i \text{ in sample} \times 100}{\text{area of peak } i \text{ in feed}}$$

$$\% \text{ Total nitrogen} = \frac{\sum \text{area of peak } i \text{ in sample} \times 100}{\sum \text{area of peak } i \text{ in feed}}$$

### Brominated Ilmenite

The ilmenite ore was taken from within 0.8 km of a point situated about 2.4 km southwest of St-Urbain and about 11.2 km north of the village of Baie St-Paul, Québec, on the north shore of the St-Lawrence River. It contained 39%  $TiO_2$ , 28%  $FeO$  and 19%  $Fe_2O_3$ . The ore was crushed to about 200 mesh and treated as follows:

In a 100-ml round bottom flask equipped with a reflux condenser, and containing 15-g of crushed ilmenite an excess of bromine (about 10 ml) was added. The mixture was heated to 58°C for 2 h, cooled, washed with 50-ml pentane to remove excess bromine. The treated ilmenite was filtered off and then washed again with pentane until the workings became colourless. The treated ilmenite was then dried with a stream of nitrogen, and used as adsorbent.

### MODEL COMPOUND STUDY

A standard solution of 18 nitrogenous compounds in toluene was prepared. Its composition is given in Table 1. This solution was pumped continuously at 0.5 ml/min into a 30 cm long x 0.4 cm I.D. column, packed with 20 g of treated ilmenite. Samples of 5-ml were collected and analyzed by gas chromatography using a 12.5 m long SE-30 capillary column.

#### RESULTS

The fate of the various nitrogenous compounds was monitored by analyzing the effluent by gas chromatography. A comparison of the results clearly shows that certain nitrogenous compounds have a greater affinity for the surface of the sulphides. Figure 1 shows the percentage of each species present in the effluent vs. the volume pumped into the column. These results show that three of the four compounds broke through the column after 5-ml compound was pumped. Tributylamine, however, was the only compound selectively removed. Thus the surface can differentiate between the various nitrogenous compounds. The same type of behaviour was observed for the other sulphide minerals.

Titanium is known to form complexes with various nitrogenous compounds (6,7). Ilmenite was treated with bromide in order to form  $TiBr_x$  and  $FeBr_x$  on the surface. Treated ilmenite was found to be a much better sorbent than untreated ilmenite. To better characterize the sorption properties of treated ilmenite a feed containing 18 model compounds was used. Figure 2 describes the fate of these 18 compounds during the run.

Compounds such as benzylamine and 2,2<sup>1</sup>-dipyridyl are extensively adsorbed and are still completely retained by the ilmenite after 150 ml has been pumped into the column. Other compounds such as carbazole are hardly adsorbed and elution occurs after 15 ml. The amount of benzylamine adsorbed is at least 20 times that of carbazole. Table 1 gives the order of elution of the 18 compounds. It is interesting to note that there seems to be a general correlation between the extent of adsorption and the basicity of the compound.

Another important feature observed in Fig. 2 is that some compounds are irreversibly adsorbed while others are reversibly adsorbed. Compounds such as indole are irreversibly adsorbed; in other words these compounds saturated the sites that were available to them and were not subsequently displaced. Conversely, compounds such as aniline are reversibly adsorbed. Their behaviour is typical of displacement chromatography where a compound is desorbed by another thus giving rise to a concentrated front that eventually elutes in the effluent. Figure 2 shows that these compounds elute in the effluent at a concentration of about three times that of the original feed. A rough mass balance indicates that these compounds are quantitatively desorbed and practically none is left on the column after the concentrated front has eluted.

## DISCUSSION

The main conclusion in this study is that sulphide minerals have a very low adsorption capacity for nitrogenous compounds. These adsorbents, however, were found to be selective. For example, pyrrhotite adsorbs about 20 times more tributylamine than carbazole or trimethylpyrrole. The more basic compounds are usually more quantitatively adsorbed which suggests that these compounds are adsorbed on the Lewis and/or Bronsted acid sites. Therefore, increasing the surface acidity should increase the amount of nitrogenous compounds adsorbed.

Ilmenite was treated with bromide to form  $TiBr_x$  and  $FeBr_x$  on the surface. These salts are known as strong Lewis acids. The capacity of the treated ilmenite is much higher than that of the natural material.

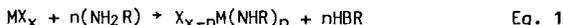
The model compound study gives some insight into the adsorption mechanism. Indeed, the adsorptive properties of the 18 compounds differ depending on their nature. The compounds can be subdivided into four classes according to their adsorption behaviour as follows:

<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
carbazole	aniline	1,2,5-trimethylpyrrole	dibenzylamine
tetrahydrocarbazole	2-phenylpyridine	n-octylamine	1-phenethyl-piperidine
indole	3,4-benzacridine	n-decylamine	2,2'-dipyridyl
3-methylindole	quinoline	2-aminochrysene	benzylamine
phenothiazine	2-methylacridine		

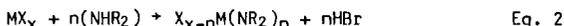
In class I all compounds are pyrrolic with active protons on the nitrogen and are weakly acidic. Carbazole is hardly retained and the rest only slightly. Due to the absence of a concentrated elution front it appears that the adsorption is irreversible. In contrast, class II compounds, being weakly basic, are more quantitatively retained but are also displaced and elute as a concentrated front. Their behaviour is typical of displacement chromatography. Classes III and IV are definitely more basic and more quantitatively adsorbed. In class IV only benzylamine has broken through.

Since classes I and III, with the exception of the trimethylpyrrole, contain an active hydrogen, a possible explanation of these results is given below.

It is well known that titanium halides will react with primary and secondary amines to form a complex (6). Nitrogenous compounds with an active hydrogen can displace halides to give complexes  $X_2Ti(NHR)_2$  or  $X_3Ti(NR_2)$ . Similar reactions are probably occurring at the surface of the treated ilmenite for titanium and iron salts.



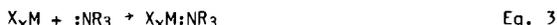
or



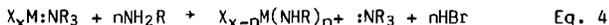
where M = Ti or Fe  
 X = halide  
 n = 1 or 2 depending on the nature of the amine  
 R = alkyl group

In this case adsorption is really a surface complexation. For purposes of this paper the term adsorption is used.

Contrary to class I, class II compounds were reversibly adsorbed. These compounds with the exception of aniline, do not have an active hydrogen on the nitrogen atom. This implies that the only mechanism of adsorption would be through the donation of the electron pair of the nitrogen to the Lewis centers. (Here, physical forces, interactions of the pi electrons with the surface, and hydrogen bond formation are neglected). The reaction can be illustrated as follows:



Delocalization of the lone pair of electrons over the ring decreases its availability for bonding. Since class II compounds are aromatics it is expected that they will form only weak bonds with the surface. This reaction is found to be reversible. The more basic compounds of classes III and IV probably displace compounds of class II according to the reaction:



Class IV compounds have the highest affinity for the surface. These compounds are basic and will react with a great portion of the sites. 2,2<sup>1</sup> dipyriddy is particularly interesting. It does not have an active hydrogen on the nitrogen atom, but is known to be a strong ligand (8). It gives stronger complexes than ligands such as primary and secondary amines. It will react with the surface in a way similar to that described by Eq. 3.

The difference in adsorption capacity between the various classes can be explained in terms of their relative basicity. The surface is made of sites of various activity. The site distribution is expected to resemble a Boltzmann distribution where the highly active sites represent only a small fraction of the sites. The extent of adsorption of the nitrogenous compounds with the surface Lewis acids will depend on the availability of the lone pair of electrons on the nitrogen atom. Compounds of class I are not basic and will react only with the highly active sites. These represent only a small percentage of the sites which explains the low level of adsorption of class I compounds. Compounds of classes III and IV are much more basic and will react with a much broader range of sites than those of class I and have a higher level of adsorption. Steric hindrance could also possibly play a role.

#### CONCLUSIONS

This study suggests that the adsorption of nitrogenous compounds on sulphide minerals and ilminite proceeds via an acid-base interaction. These adsorbents would successfully remove basic nitrogenous compounds, but not the acidic nitrogenous compounds. This implies that the effective capacity of the adsorbent will vary with the feed composition. This uncertainty would inhibit the use of such an adsorbent for routine use with feeds of changing composition such as petroleum feedstocks.

Therefore, the waste minerals investigated are not feasible adsorbents for industrial use. However, this study suggests a new approach to design an effective adsorbent. The ideal adsorbent would separate these compounds by a non-acid/base interaction which would allow both acid and basic nitrogenous compounds to be separated indiscriminantly. Such an adsorbent has been identified and the results will be published soon.

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TABLE 1  
ORDER OF BREAKTHROUGH FOR MODEL COMPOUNDS

Curve No. on Fig. 2	Compound	Initial Concentration ppm	Volume at which 10% is reached (mL)	PKa*
1	Carbazole	25.24	1	
2	3-methylindole	26.74	20	
3	Phenothiazine	29.60	25	
4	Indole	29.37	31	
5	Tetrahydrocarbazole	27.70	30	
6	Aniline	30.12	45	4.63
7	2-phenylpyridine	24.26	45	
8	2-aminochrysene	13.90	45	
9	1,2,5-Trimethylpyrole	28.20	48	
10	3,4-benzacridine	7.85	51	
11	n-octylamine	32.62	55	10.65
12	n-decylamine	27.08	60	10.63
13	Quinoline	32.02	65	4.90
14	2-methylacridine	18.40	100	
15	Benzylamine	39.79	100	9.33
-	1-phenethylpiperidine	22.88	-	
-	2,2'-dipyridyl	55.58	-	
-	Dibenzylamine	26.48	-	

\*CRC - Handbook of Chemistry and Physics, R.C. Weast Ed., CRC press 1976, 57th edition.

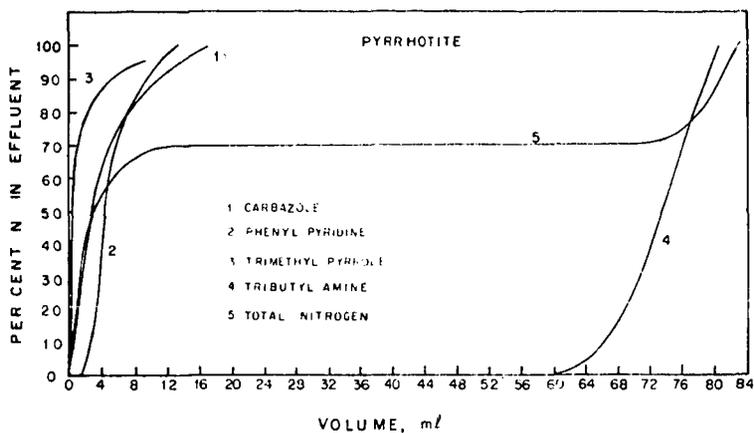


Fig. 1 - Adsorption of nitrogenous compounds on pyrrhotite

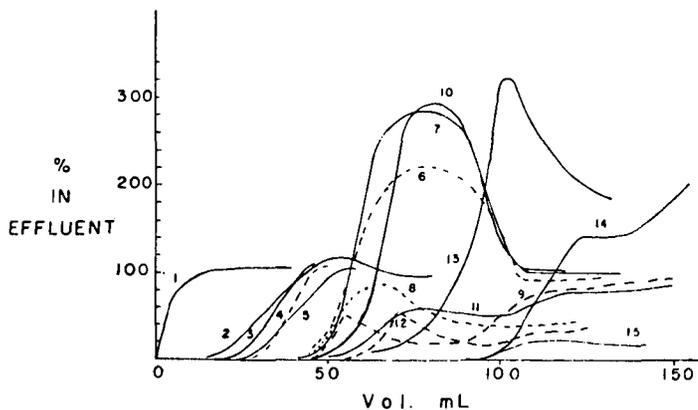


Fig. 2 - Breakthrough curves of individual compounds 1) carbazole; 2) 3-methylindole; 3) penothiazine; 4) indole; 5) tetrahydrocarbazole; 6) aniline; 7) 2-phenylpyridine; 8) 2-aminochrysene; 9) 1,2,5-trimethylpyrrole; 10) 3,4-benzacridine; 11) n-ocylamine; 12) n-decylamine; 13) quinoline; 14) 2-methylacridine; 15) benzylamine; not broken through: dibenzylamine; 1 phenethylpiperidine; 2,2<sup>l</sup> dipyridyl.