

Energy, Mines and Énergie, Mines et Resources Canada Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology Centre canadien de la technologie des minéraux et de l'énergie

REMOVAL OF SYNTHETIC CRUDE NITROGENOUS COMPOUNDS USING WASTE MINERALS

G. Jean, M. Poirier, and H. Sawatzky

APRIL 1984

ENERGY RESEARCH PROGRAM ENERGY RESEARCH LABORATORIES ERP/ERL 84-10 (OP,J) 484

ABSTRACT

REMOVAL OF SYNTHETIC CRUDE TYPE NITROGENOUS COMPONENTS USING WASTE MINERALS, G.Jean, M. Poirier and H. Sawatzky

In the near future synthetic crudes will play an increasingly important role as prime energy sources. These crudes are much different than convenlional crudes and new technologies will be required to make optimum use of these sources.

Synthetic crudes contain a much higher nitrogen level than conventional crudes and thus will require severe hydrotreating. The high capital investment and operation costs of the hydrotreating process suggest that hydrotreating should be kept to a minimum. Removing the nitrogenous fraction by non catalytic methods may be a better alternative.

In this study several waste minerals were tested as sorbents for the removal of nitrogenous components. The results show that some nitrogenous components can be selectively removed with some waste minerals. The extent of adsorption strongly depends on the nature of the nitrogenous compounds. The adsorption proceeds via an acid-base interaction.

٩. ١

Séparation des composés azotés typiques des huiles synthétiques par des déchets miniers

par

G. Jean*, M. Poirier* and H. Sawatzky**

Résumé

Sous peu les huiles synthétiques joueront un rôle important comme source d'énergie. Ces huiles diffèrent des huiles conventionnelles et nécessitent une technologie nouvelle pour leur valorisation.

Ces huiles contiennent beaucoup plus de produits azotés et doivent être sévèrement hydrotraitées. Les coûts élevés d'équipement et opération du procédé d'hydrotraitement suggèrent que ce procédé devrait être évité si possible. Donc enlever la fraction azotée par une méthode non-catalytique offre une possibilité attrayante.

Dans cette étude, plusieurs déchets miniers ont été testés comme sorbants. Les résultats montrent que certains produits azotés sont sélectivement séparés. Le degré d'adsorption dépend de la nature des composés. L'adsorption se fait via un interaction acide-base.

٠,

- iii -

١,

.

•

-

-

CONTENTS

•

.

Abstract	••• •	••••	• • • •	• • • •	• • • •	••	• • •		• • • •	•••	• • •	• • •	• • •	•••	•••	• • •	• •		• • •	••	i
Résumé	• • • • •	• • • • •	• • • •	• • • •	• • • •	• • •	•••	• • • •	• • •	• • •	• • •	• • •	• • •	•••	•••	• • •	• • •	• •	• • •	••	ii
Contents	• • • • •	• • • •	• • • •	• • • •	• • • •	• • •	• • •	• • • •		•••	• • •	• •	• • •	•••		• • •	•••		•• •	•••	iii
Introducti	.on	• • • •	• • • •	• • • •	• • • •	• • •	•••	• • • •	• • • •	• • •	• • •	•••	• • •	• • •	•••	• • •	•••	••	• • •	••	1
Experiment	al	••••	• • • •	• • • •	• • • •	• • •	• • •	• • • •		• • •	• • •	•••	•••	• • •		• • •	• • •	••		••	2
Results	••••	• • • •	• • • •	• • • •	• • • •	• • •	•••	• • • •	• • • •		• • •	• • •	• • •	• • •		• • •	•••	••	•••	••	3
Discussion	•••••	• • • •	• • • •	• • • •	• • • •	• • •	• • •	• • • •		• • •	• • •	• • •	• • •	• • •		• • •	•••	••	• • •		5
Conclusion		• • • •	• • • •	• • • •	• • • •	•••	• • •	• • • •	• • • •	• • •	• • •	• • •	• • •	• • •	• • •	• • •	• • •	••	• • •	••	8
References	· · · ·	• • • •	• • • •	• • • •	• • • •	• • •	• • •	• • • •		• • •	• • •	•••	• • •	•••			•••	••		••	9

Tables

No.	1	Order of elution of model compounds	10
No.	2	Composition of standard feed	10

Figures

No.	1	Breakthrough	curves	of	model	compounds	on	pyrrhotite	11
No.	2	Breakthrough	curves	of	model	compounds	on	treated ilmenite	12

GENERAL PAPERS - POSTER SESSION PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC. AMERICAN CHEMICAL SOCIETY PHILADELPHIA MEETING, AUGUST 26-31, 1984

REMOVAL OF SYNTHETIC CRUDE NITROGENOUS COMPOUNDS USING WASTE MINERALS

ΒY

G. JEAN, M. POIRIER, and H. SAWATZKY ENERGY RESEARCH LABORATORIES CANMET. OTTAWA, CANADA

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

٠.

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 (FeS₂), sphalerite (ZnS), and chalcopyrite (FeCuS₂).

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:

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% TiO₂, 28% FeO and 19% Fe₂O₃. The ore was crushed to about 200 mesh and treated as follows: In a 100-mL round bottom flash 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 compositon 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. Tributyl amine, 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.

- 3 -

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 2,2¹-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 2 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.

- 4 -

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

- 5 -

In class 1 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 benylamine has broken through.

Since classes I and III, with the exception of the trimethyl pyrrole, contain 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.

$$MX_x + n(NH_2R) - X_{x-n}M(NHR)_n + nHBR$$
 Eq. 1

00

$$MX_x + n(NHR_2) - X_{x-n}M(NR_2)_n + nHBr$$
 Eq. 2

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

- 6 -

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:

$$X_xM + :NR_3 - X_xM:NR_3$$
 Eq. 3

Delocalization of the one 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:

$$X_x M: NR_3 + nNH_2 R - X_{x-n} M(NHR)_n + :NR_3 + nHBr Eq. 4$$

Class IV compounds have the highest affinity for the surface. These compounds are basic and will react with a great portion of the sites. 2,2¹ dipyridyl 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.

- 7 -

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. 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.

- 8 -

REFERENCES

ı

1.	Jewel, D.M., and Snyder, R.E., J. Chromatog., <u>38</u> , 351 (1968)
2.	Ford, C.D. et al. Anal. Chem., <u>53</u> , 831 (1981)
3.	Guerin, M.A. et al. Environ. Res., <u>23</u> , 42 (1980)
4.	Audeck, C.A., PREPRINTS, Div. of Petrol. Chem., ACS, <u>27</u> , 998 (1982)
5.	Jean, G.E. Ph.D. Thesis, University of Western Ontario (1983)
6.	Cotton, F.A. and Wilkinson, G. <u>Advanced Inorganic Chemistry</u> , 3rd ed., Interscience Publishers, New York, (1972), p. 813
7.	Ben Kovski, V.G. and Olzseva, M.D., Chem. Techn. of Fuel and Oil, 474 (1979)
8.	Huhey, J.E., <u>Inorganic Chemistry: principles of structures and reactivity</u> , Harper and Row, Publishers, New York (1972)

- 9 -

÷

Compound	ppm N
aniline	30.12
1,2,5-trimethylpyrrole	28.20
benzylamine	39.79
n-octylamine	32.62
quinoline	32.02
n-decylamine	27.08
indole	29.37
3-methylindole	26.74
2,2 ¹ -dipyridyl	55.58
2-phenylpyridine	24.26
1-phenethylpiperidine	22.88
dibenzylamine	26.48
tetrahydrocarbazole	27.70
carbazole	25.24
2-methylacridine	19.40
3,4-benzacridien	7.85
2-aminochrysene	13.90
phenothiazine	29.60
Total N concentration	518.21

TABLE 1 COMPOSITION OF STANDARD SOLUTION

		URDER UF BREAKTH	ROUGH FUR MODEL L	COMPOUNDS					
Curv	e No.	Volume at which							
on			10% is reache	ed	Proton				
Fig.	2	Compound	(mL)	PKa	Affinity				
1		Carbazole	1						
2		3-methylindole	20						
3		Phenothiazine	25						
4		Indole	31						
5		Tetrahydrocarbazole	30						
6		Aniline	45	4.63	213.5				
7		2-phenylpyridine	45						
8		2-aminochrysene	45						
9		1,2,5-Trimethylpyrole	48						
10		3,4-benzacridien	51						
11		n-octylamine	55	10.65					
12		n-decylamine	60	10.63					
13		quinoline	65	4.90	228.4				
14		2-methylacridine	100						
15		Benzylamine	100	9.33					
		1-phenethylpiperidine							
-		2,2 ¹ -dipyridyl	-						
-		Dibenzylamine	-						

TABLE 2 ORDER OF BREAKTHROUGH FOR MODEL COMPOLINDS

*,•

.

٠.

.



Fig. 1 - Adsorption of nitrogenous compounds on pyrrhotite



Fig. 2 - Breakthrough curves of individual compounds 1) carbazale;2) 3-methylindole;
3) phenothiazine; 4) indole; 5) tetrahydrocarbazole; 6) aniline; 7) 2-phenylpyridine;
8) 2-aminochrysene; 9) 1,2,5-trimethylpyrrole; 10) 3,4-benzacridine; 11) n-octylamine;
12) n-decylamine; 13) quinoline; 14) 2-methylacridine; 15) benzylamine; not broken through: dibenzylamine; 1 phenethylpiperidine; 2,2¹ dipyridyl