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DISTRIBUTION OF HEAVY METALS IN VARIOUS ORGANIC AND MINERAL FRACTIONS OF ATHABASCA OIL SANDS

by

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Abstract

Metals in crude oils arise from several sources. Produced oil will contain metal contributions from organic matter associated with the reservoir rock, from minerals leached during migration, after emplacement in reservoirs and from contamination during production and shipment. In sedimentary organic matter both organic as well as inorganic associations of the metals are involved, and often they interact directly or indirectly with each other. Organic associations of the metals are usually in the form of organo-metallic complexes such as metal porphyrins or as metal humates. Sometimes substantial concentrations of metal complexes are incorporated into the organic matter of fossil fuels. Metals in fossil fuels usually have an adverse affect on processing, product properties as well as posing environmental problems. However, the study of their distribution in petroleum and source rocks often leads to useful information regarding the transformation of organic matter into crude oils.

In this investigation we have analyzed a number of Athabasca oil sands derived samples to estimate the distribution of heavy metals within organic and inorganic phases. The work included HCl/HF acid demineralized oil sands feedstock and tailings solids, humic matter from oil sand feedstock and various tailings streams, heavy metal mineral concentrates containing strongly adsorbed insoluble organic matter, bitumen, asphaltene, cokes and fly ash samples obtained from the processing of bitumen. The metal concentrations have been expressed as per g of total organic carbon instead of per g of total sample weight in order to make more meaningful comparisons of the data. The elemental concentrations range over more than six orders of magnitude. Attempts have been made to interpret the data in terms of organic or inorganic association of the metals, as well as the relationship of the humic matter to the toluene extractable organic matter from oil sands.

Introduction

Studies on the occurrence of metals in crude oils and source rocks are of interest to geologists, chemists and chemical engineers. Metals and metallo-organic compounds are often correlated with the origin of the crudes.¹ Organic substances play a dominant role in geochemical cycling, especially in the local concentration of trace metals. Metal-organic and organo-metallic species in sediments may originate from the biomass without major chemical changes, or they may be formed during sedimentation and/or diagenesis from organic molecules and metal ions derived from different biogenic (biomass) and abiogenic sources (weathering of minerals). Thus, in many of these

geochemical cycles inorganic as well as organic associations of the metals are involved, and often they directly or indirectly interact with each other.²

The occurrence of metals in various organic and inorganic fractions of oil sands has important implications for the extraction, processing, and upgrading of bitumen and synfuels. Their occurrence as organo-metallic complexes in the organic phase, or in association with minerals or clays, has important consequences for their behaviour and influence in processing.

In this investigation, we have analyzed a number of samples for Ca, Al, Fe, Ti, Mg, V, Ni, Cu, Cr and Zr using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

These included samples of oil sand feedstock, overburden, solids from tailings streams, and oil sands derived organic matter fractions such as bitumen, asphaltenes, humic matter fractions, coke and fly ash samples from oil sand operations.

Experimental Methods

Samples. Samples of oil sand feedstocks, overburden, bitumen, cokes and fly ashes were obtained from the Alberta Research Council sample bank. Asphaltenes were precipitated from bitumen using n-pentane³, oil phase solids (OPS), the heavy metal minerals concentrate containing unextractable organic matter, were isolated using an oil phase agglomeration technique reported elsewhere.⁴ Humic acids (HA) were extracted using NaOH or a mixture of NaOH+Na₄P₂O₇ as reported earlier.⁵ Insoluble organic matter was enriched by dissolving the mineral matter in HCl/HF, which yielded acid demineralized samples.^{4,6,7}

Ash Content. Ash content of various samples was determined by heating at 390±10°C to constant weight.⁸

Analysis. Ashed samples were analyzed using quantitative Inductively Coupled Plasma Atomic Emission Spectroscopic method (ICP-AES) for the estimation of SiO₂, Ca, Mg, Al, Ti, Zr, V, Ni, Cu, Cr, and Fe.

Table 1. Abbreviations

Abbreviation	Description
ND	Not determined
HA	Humic Acid
FA	Fulvic Acid
DM	HCl/HF demineralized
OS	Oil Sands
OB	Overburden
W/W %	Weight/Weight %
HA-Bit.free SS	Humic acid and bitumen free sludge solids
SCT	Syn crude centrifuge tailings
OPS	Heavy metal minerals concentrate obtained using oil phase agglomeration
TOC	Total organic carbon

Results and Discussion

A number of samples derived from Athabasca oil sands were analyzed in order to analyze the distribution of heavy metals within the organic and inorganic (mineral) phases. These included HCl/HF demineralized oil sand feedstocks and tailings solids, humic matter from oil sand feedstock and various tailings streams, heavy metal mineral concentrates obtained using oil phase agglomeration techniques⁴; bitumen, asphaltenes, coke and fly ash samples.

The organic matter associated with oil sands and related materials can never be completely free from inorganic contamination. This makes the determination of the chemical nature of heavy metal species in these materials very difficult. For example it is difficult to estimate the amount of heavy metal content associated with either the organic matter or in association with mineral matter. Uncontrollable amounts of mineral impurity in the concentrated organic matter results in dilution of calculated amounts of the trace element content of the mineral free organic matter. In order to normalise the data, the concentrations have been expressed as per g of total organic carbon (TOC) rather than per g of sample. This methodology allows direct comparison of the data from different samples. These data are listed in Tables 2.

To indicate the concentration ranges of trace elements in various oil sands components, the data has been compiled in Figures 1 and 2. A comparison of the data in the Table and Figures lead to a number of conclusions:

1. Elemental concentrations for the same elements range over more than six orders of magnitude, i.e. from several parts per billion to several weight percent for the different samples.
2. With the exception of V and Ni, the elements are enriched in the OPS fractions. This is consistent with the results of our previous work whereby we have demonstrated that heavy metal minerals associated with oil sands and related feedstocks can be enriched by oil phase agglomeration employing heavy oils as collectors.⁹
3. Compared to humic matter fractions, asphaltenes show significantly higher contents of V and Ni which are usually found in the form of porphyrin or non-porphyrin complexes in sedimentary organic matter.¹⁰ These metals get concentrated in cokes and fly ash samples as a result of the coking process. Much higher concentrations of Ni in OPS as compared to asphaltenes, suggest that part of the Ni might be associated with the mineral matrix.

4. Humic matter fractions (HA and acid demineralized samples) show significantly lower contents of Ni and V, than asphaltenes. Ni/V ratio is also significantly lower in humic matter fractions than in bitumen and asphaltenes. Ni and V complexes are usually concentrated in the heavier more polar fractions.¹¹ Therefore it is probable that these elements do not have the same origin in the two types of organic matter. This leads to the hypothesis that this humic matter is not a precursor to bitumen and that both fractions have independent origin.
5. Cu and Cr concentrations are much lower in bitumen and asphaltenes compared to humic matter fractions, indicating the latter's greater Cu and Cr metal complexation capacity. Also, compared to organic matter fractions, OPS show significantly higher contents of Cu and Cr. This result is in accordance with the presumed association of these metals with both organic and inorganic phases.
6. The relatively high concentrations of Ca and Al in the humic matter fractions suggests the presence of metal humates in these samples. This is consistent with our previous results in which we have demonstrated the presence of metal humates in oil sands and related feedstocks.⁵
7. Fe, Ti and Zr are very low in bitumen and asphaltenes as compared to the OPS and high ash humic matter fractions. This suggests that these metals could be derived from the mineral matrix in these samples.
8. The V/Ni index varies considerably. Bitumen, asphaltenes and acid demineralized oil sand and overburden samples have the highest V/Ni ratio. The V/Ni index for humic matter fractions is about one third of the value for bitumen and asphaltenes. This variation could be because of the fact that both inorganic as well as organic associations of the metals could be involved in these samples. It is also possible that the metals in various samples investigated could have different origins.

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- Table 1. List of Abbreviations
- Table 2. Chemical analyses of bitumen & humic matter fractions from oil sand related materials

Table 2. Chemical analysis of bitumen and humic matter fractions from oil sand related materials.

Sample ID	Ash w/w %	C** w/w %	V/Ni	Elemental analysis of ash (based on per g of carbon)										
				w/w%						ppm**				
				Al	Fe	Ti	Ca	Zr	Cu	Cr	V	Ni		
Bitumen ³	0.5	83	4.5	0.1	0.02	0.01	26	5	1	0.4	295	65		
Asphaltenes ³	2.4	77	4.8	0.3	0.1	0.05	430	23	4	1	1380	290		
Syncrude Coke	8.0	77	2.2	0.7	0.6	0.15	1770	52	10	17	1350	615		
Suncor Coke	3.4	83	2.6	0.3	0.2	0.06	1760	22	4	12	820	310		
Syncrude Fly Ash	17.7	67	2.9	2.4	2.0	0.45	4230	140	32	42	2500	870		
Suncor Fly Ash	39.7	51	2.6	7.0	5.5	2.0	3.4%	650	100	220	2.3%	0.9%		
HA-1 from OS	1.3	65	1.4	0.02	0.02	0.09	15	130	40	3	7	5		
HA-2 from OS	7.4	60	1.4	2.6	0.03	0.03	350	90	170	25	90	62		
HA-3 from SSS	8.9	65	1.3	2.2	0.5	0.6	180	220	50	92	130	102		
DMOS	30.1	43	3.7	7.8	7.5	1.1	2200	400	230	120	199	53		
DMOB	8.9	61	5.8	1.6	0.6	0.5	500	200	23	16	128	22		
DMSCT	26.1	41	2.9	9.5	2.0	0.7	1600	1700	40	70	146	51		
DMSSS	12.4	49	0.7	0.5	1.9	8.1	400	1200	203	220	170	261		
OPS-1	57.8	30	1.3	4.1	27.3	6.6	ND	2100	600	0.5%	800	600		
OPS-2	51.6	33	1.2	9.7	20.6	8.4	ND	3800	600	3.0%	600	500		

* The results shown are an average of the data from at least three samples.

** Most of the data was converted to the nearest whole number.

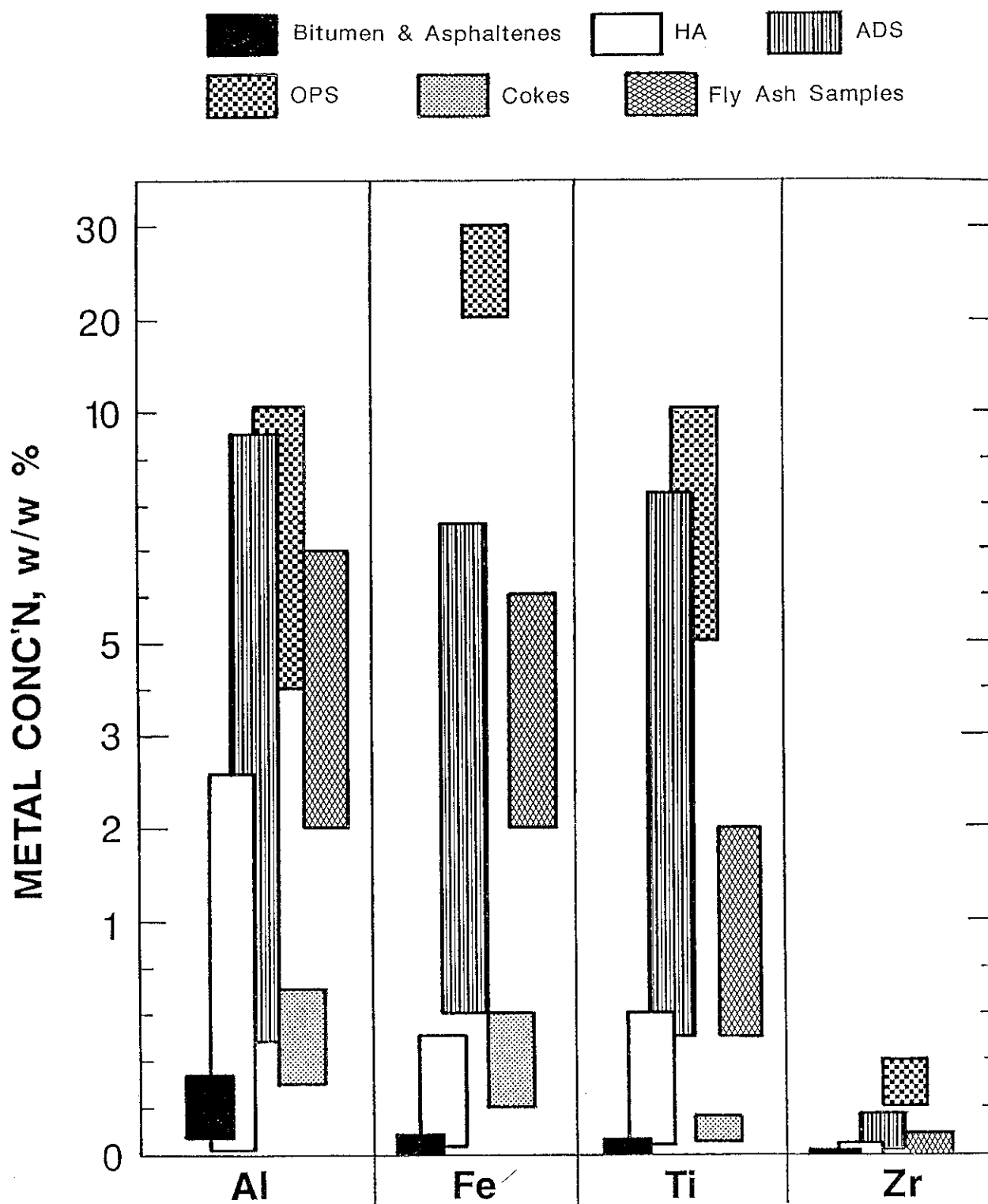


Figure 1. Ranges of Al, Fe, Ti, and Zr concentrations in various components of oil sands

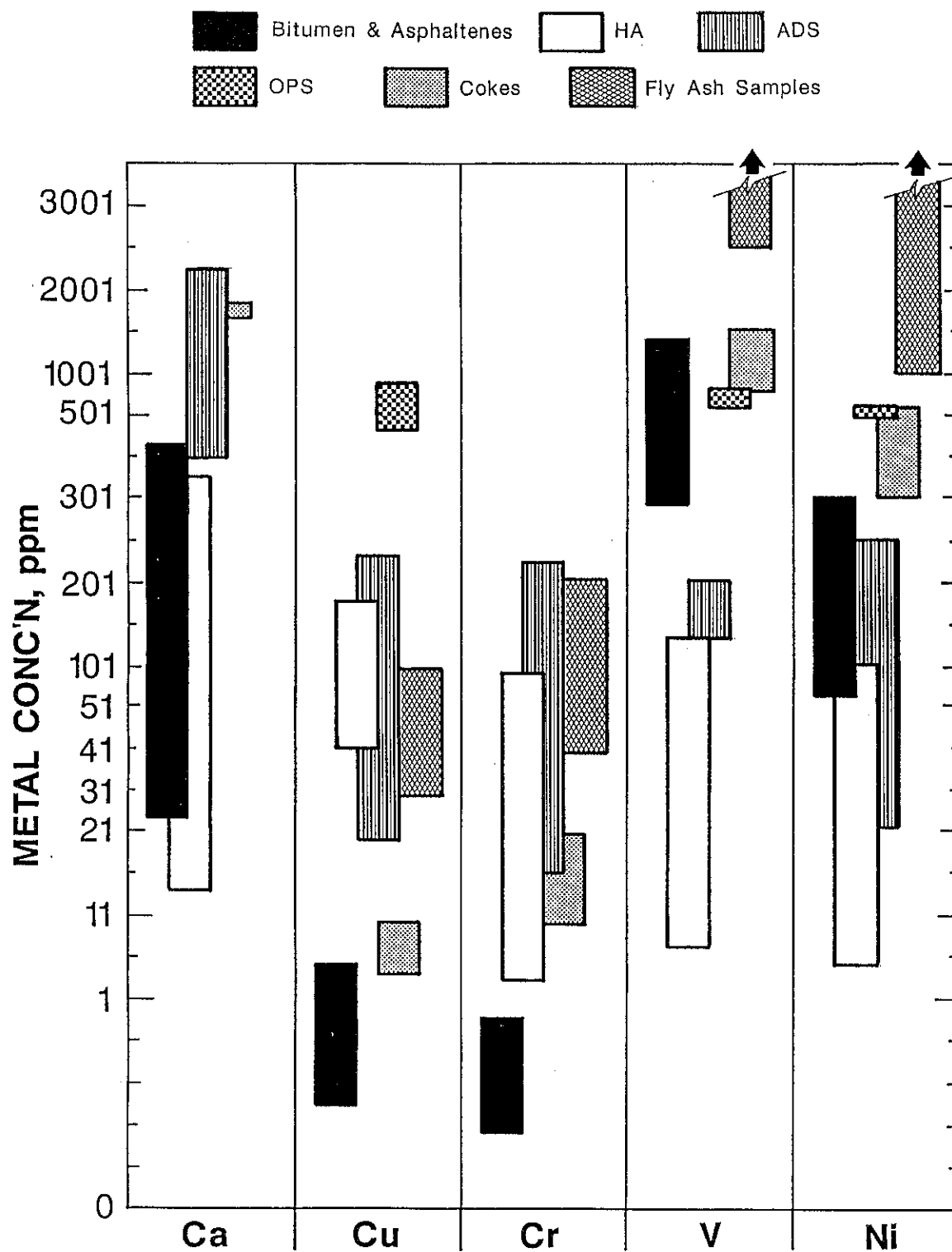


Figure 2. Ranges of Ca, Ni, Cu, Cr and V Concentrations in various components of oil sands