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VANADIUM COMPOUNDS IN ASHES FROM A CFBC FIRING 100% PETROLEUM COKE

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Natural Resources Canada | Ressources naturelles Canada

Canada

Vanadium from Petcoke

- Petroleum coke is the only common feedstock with high Vanadium contents
- It is increasingly burned in large CFBC boilers (100-250 MWe) such as NISCO
- Fuel grade petcoke is always also high sulphur
- Ashes are unique in that they don't contain dehydroxylated clays

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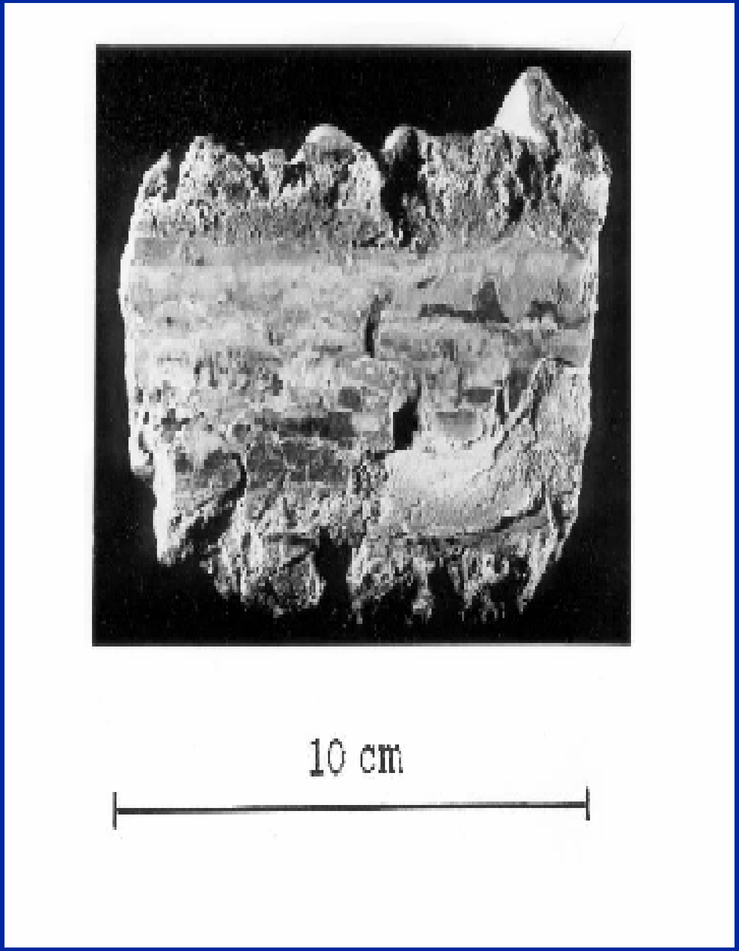
Petrleum Coke



- Petcoke is a by-product of crude refining process
  - Over 22 million tons of petcoke is produced in the US annually
  - Ideal fuel for FBC systems but problems are possible
    - Corrosion/fouling
    - High Nitrogen and Sulfur content
    - Possible Leachates from ash

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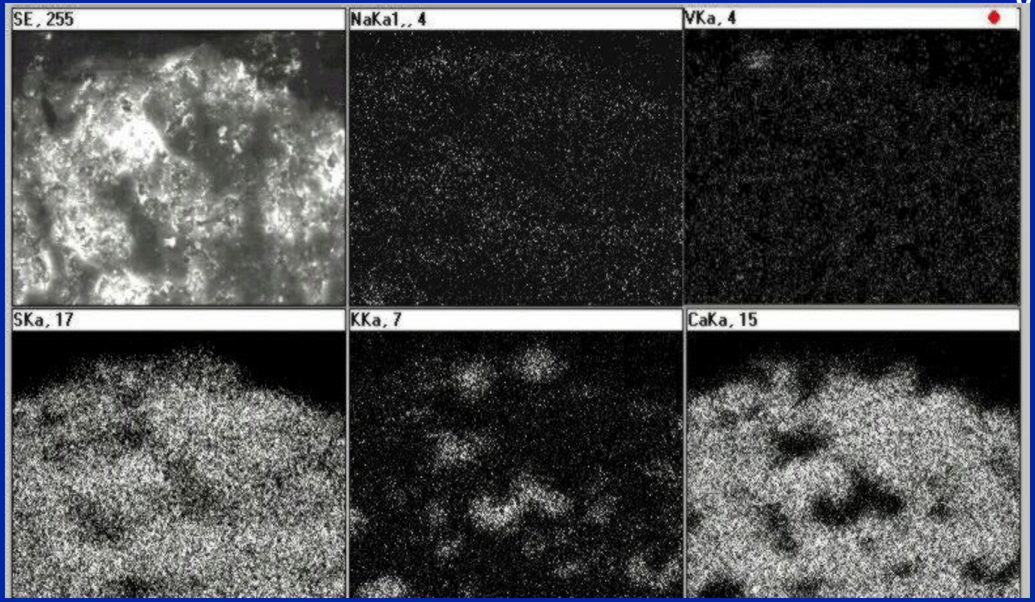
Petroleum Coke as fuel



- Fouling has been seen with boilers firing petcoke
  - However, Anthony and his co-workers have unequivocally shown this is a low ash and not a V problem
  - V is always associated with Ni at a constant V:Ni ratio and always present as Ca vanadates

Petcoke as Boiler Fuel

- The high V content of petcoke (sometimes several per cent in the ash), and Ni can be a concern
  - Chisman Creek had 500,000 tons of coal/coke ash from a PC boiler
  - V, Ni and Se were found in the ground water and Chisman Creek became a superfund site
  - The difference between PC and FBC systems firing Petcoke is limestone

GWF Power Systems

- GWF operates 6 CFBC in the Bay area in California
  – A sample of ash from one of these boilers firing 100% petroleum coke was examined.
  – The primary purpose of the investigation was to examine the V speciation in the ash because this affects V solubility

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Analysis of Feedstocks

	Kaolin	Limestone	CFBC ash - UT	CFBC ash analysis - CETC	
SiO_2	45.60	2.9	8.07	9.14	8.57
Al_2O_3	37.60	0.4	4.34	4.23	4.27
Fe_2O_3	0.40	0.2	1.96	1.71	1.78
CaO	0.60	47.6	41.95	43.98	43.70
MgO	0.60	5.5	6.19	6.03	5.89
Na_2O	0.15		0.92	0.75	0.73
SO_3			28.9	28.8	24.64
K_2O	0.15				
V_2O_5			1.16	0.96	0.98
LOI	13.25	42.5	5.0	6.03	6.55
Sum	100.0	99.1	98.5	100.67	97.11

Waste Extraction Test

- A waste extraction test was carried out
  - Sample was treated with a 0.2 M sodium citrate solution
  - V in liquid was 0.071 mg/L which is equivalent to 0.013% of V in the sample and is negligible
- Next Phase Separation was performed on the ash

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QXRD Examination of Ash

Sample	% of initial sample	V% (neutron activation)	XRD results	
			Major	Minor
1: Original CFBC ash	100	0.61	Anhydrite ($CaSO_4$) Lime (CaO) Periclase (MgO)	Unidentified small peaks

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Phase Separation-QXRD

Sample	% of initial sample	V % (neutron activation)	XRD results	
			Major	Minor
2: D-W(40 min)-D	12	0.58		
3: D-W(40 min)-W(4.3 h)	27	1.46	Anhydrite Periclase Gehlenite ($2CaO.Al_2O_3.SiO_2$) Calcite ($CaCO_3$)	Unidentified minor peaks
4: W(7.3 h)	38	1.24	Gehlenite Anhydrite Periclase Calcite Quartz (SiO_2)	Sulphur (S) Unidentified minor peaks

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Phase Separation - QXRD

Sample	XRD results	
	Major	Minor
5: W(72 h)-W(96 h)	Ettringite $(Ca_6Al_2(SO_4,SiO_4,CO_3)(OH)_{12}\cdot 26 H_2O)$ Gehlenite Periclase Quartz Calcite	$Ca_2V_2O_7.2H_2O$ $Fe_4(VO_4)\cdot 5H_2O$ $Mg_2V_2O_7$ $Na_4V_2O_7\cdot 18H_2O$

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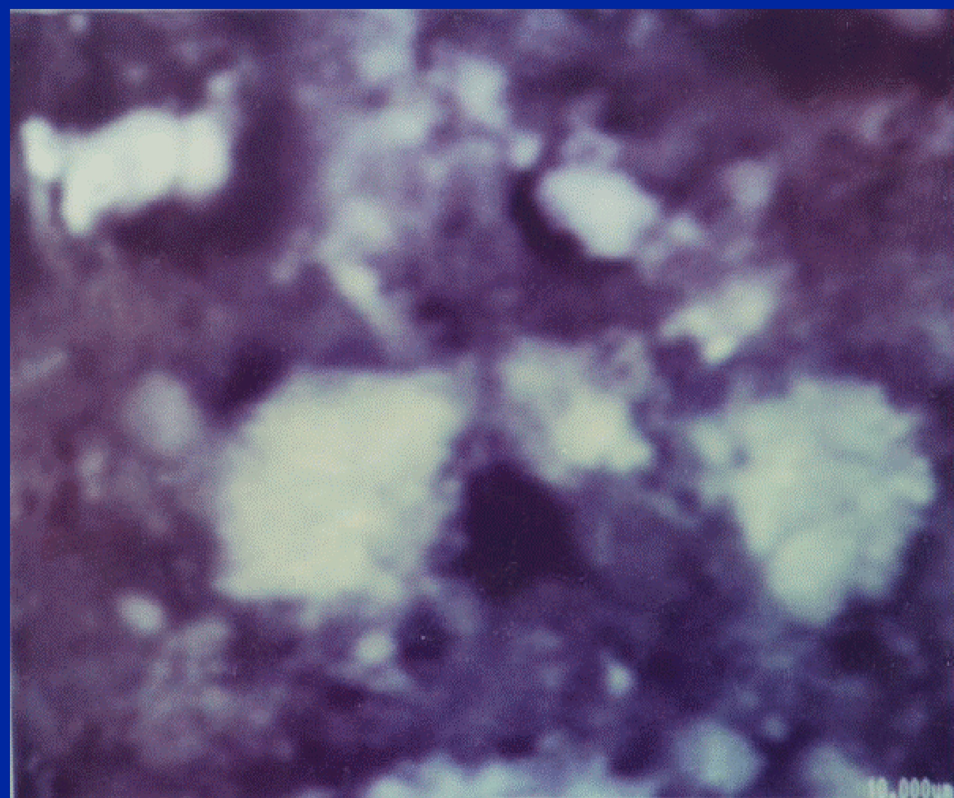
SEM of Sample 3



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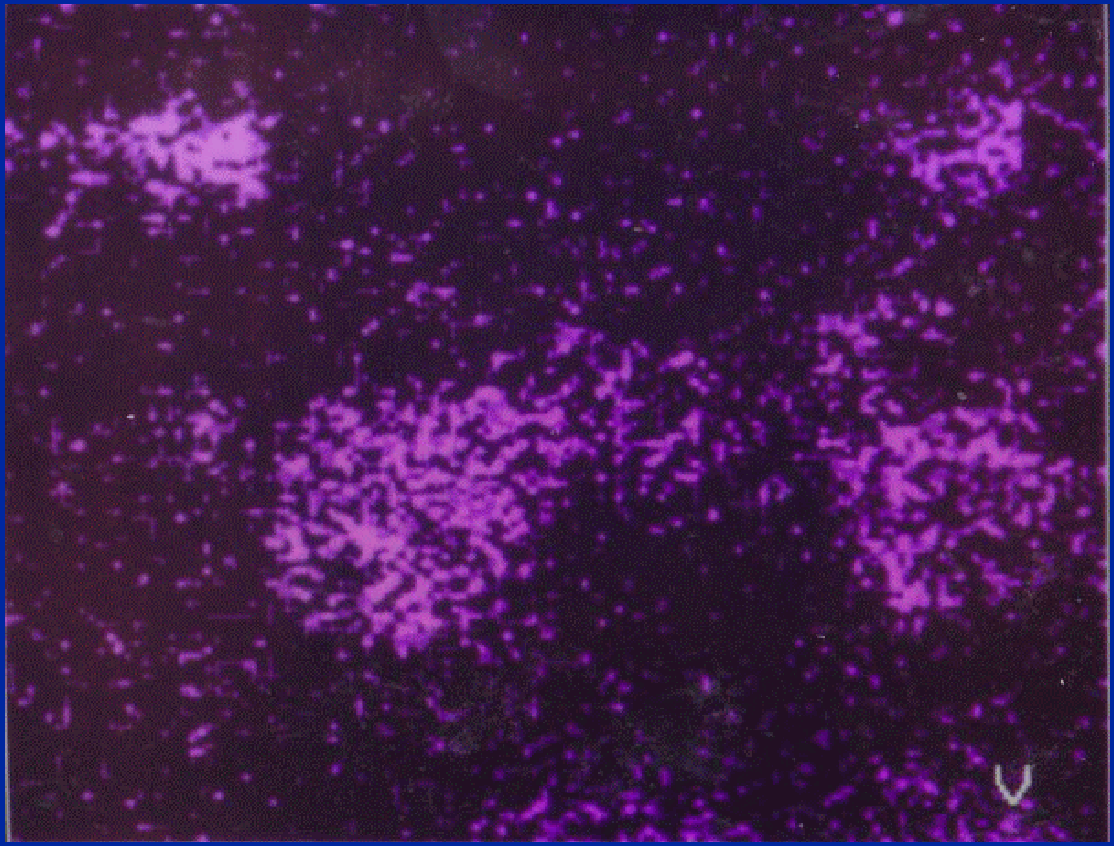
Sample 3 under SEM/EDX



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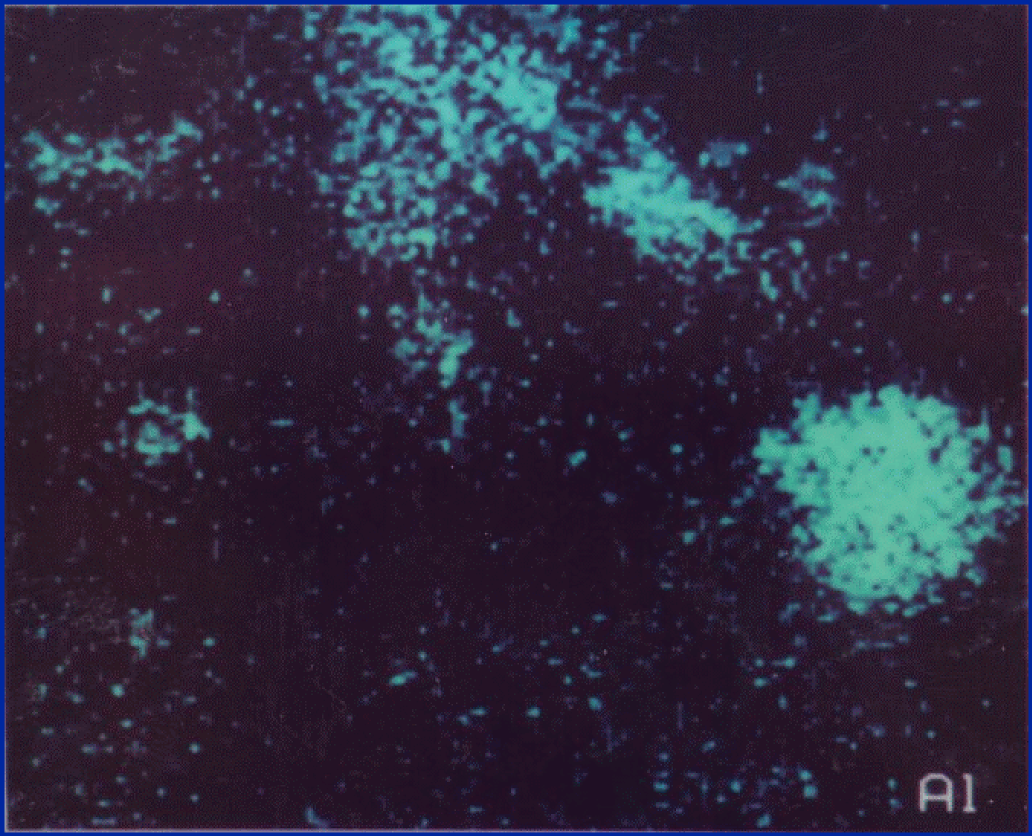
Sample 3 under SEM/EDX



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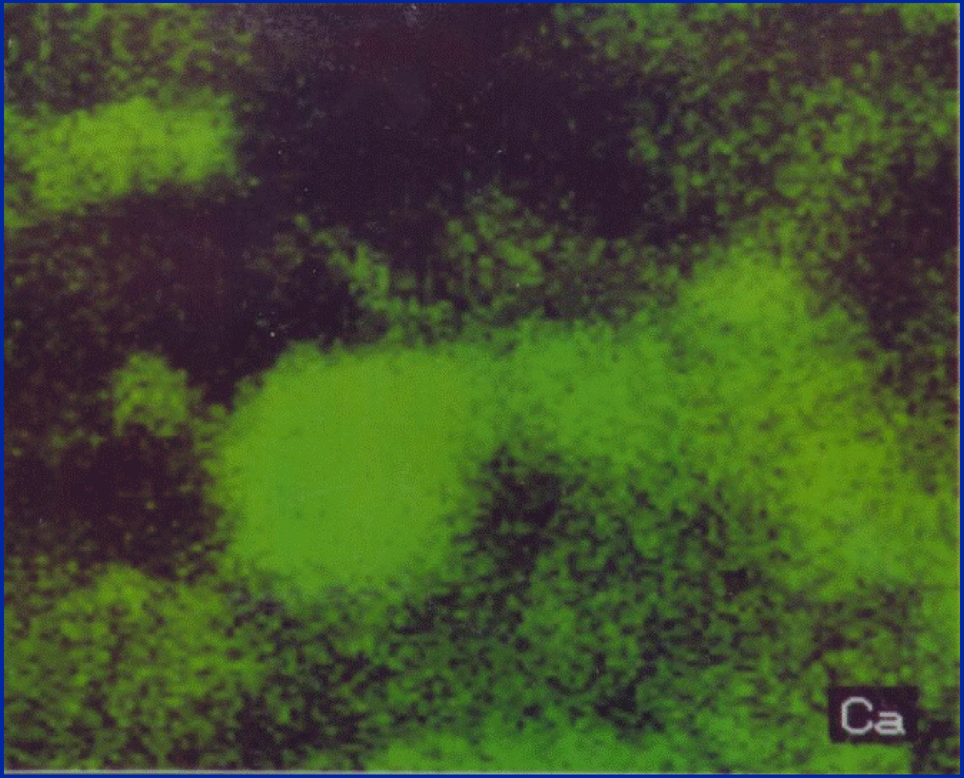
Sample 3 EDX



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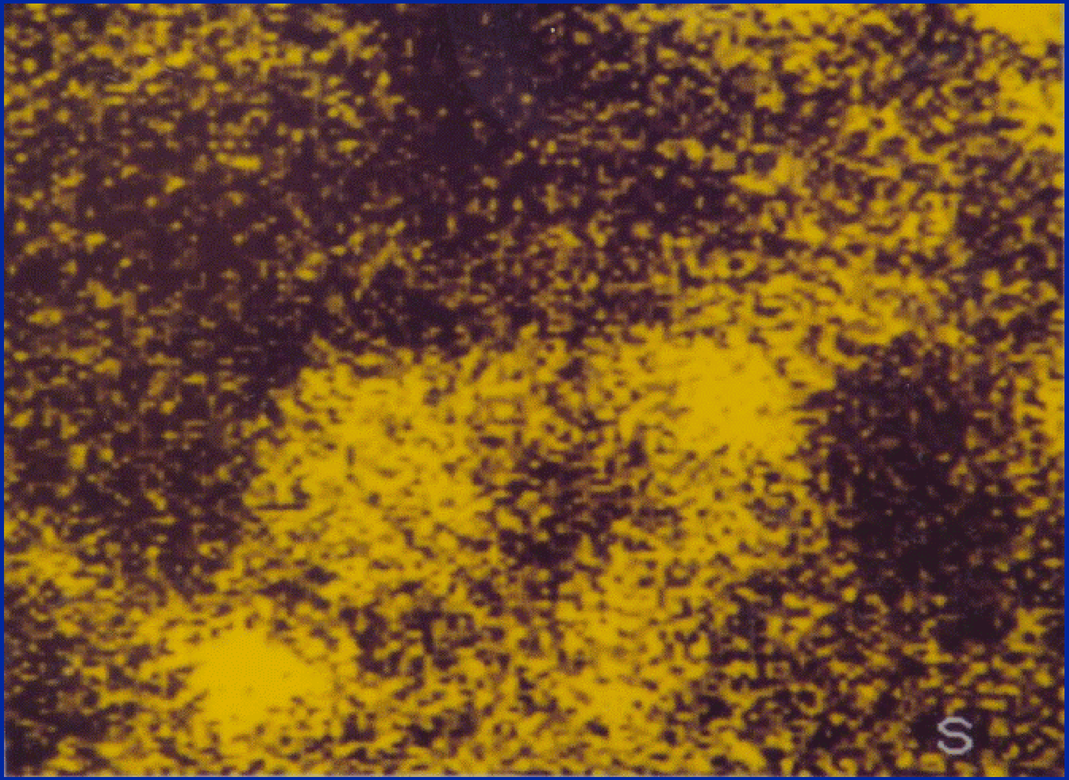
Sample 3 under EDX



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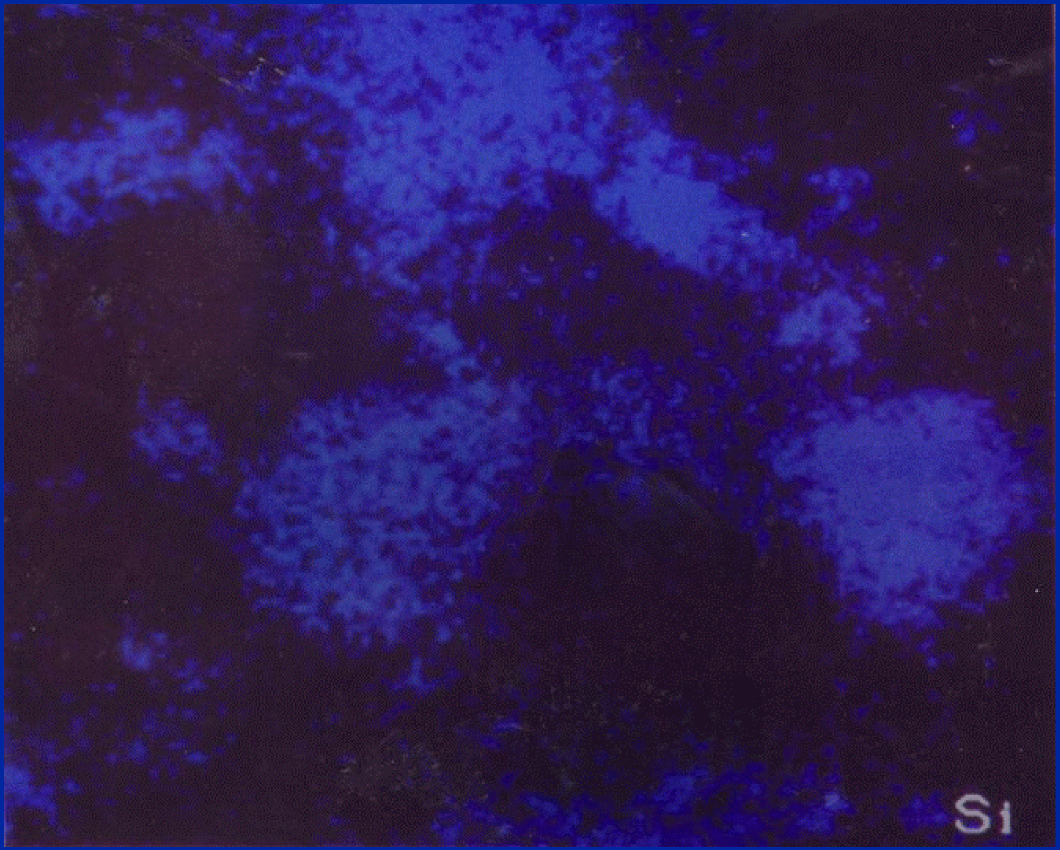
Sample 3 under EDX



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Conclusions from SEM/EDX

- No separate particles revealing on V and Ca
- Vanadium always appears in minor proportions with large amounts of Ca and other elements (Ca, S, Al, Si and Fe)
  - Does not support the idea of V oxides
  - Does support the idea of Ca vanadates and other compounds

Conclusions

- Phase separations were relatively unsuccessful in concentrating V
  - enrichment of 2.5
- Extended XRD examination suggested $Ca_2V_2O7.2H_2O$ and possibly $Na_3V_2O_3(SO_4)_4$.
- A caveat for the researcher working with petcoke fired boilers is to check for additives, 100% firing of petcoke should not be assumed, and additives are frequently used to prevent fouling properties

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Conclusions

- WET extractions produced very little change in the sample besides hydrating CaO
- Vanadium was still present as Ca Vanadium Oxides although different ones than seen previously
- Only 0.013% of V was lost

Conclusions

- Elimination of CaO/$CaSO_4$ led to much higher V contents in the leachate 12% of V was lost
- The bulk of the V was present in the 5+ oxidation state, and it is believed that it was present mainly as (Mg, Ca, Na, K, Fe)$V_2O_7.xH_2O$ and perhaps some $Fe_4(VO_4)_4$