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Low temperature plasma ashing of coal for quantitative mineral analysis

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ABSTRACT
Understanding the nature and distribution of minerals in coal yields important information on the geological formation of coal and effects of minerals on coal utilization including combustion and carbonization. Specifically, understanding the environmental impacts of coal mining and its combustion by-products is essential information for improving coal-fired power plant technology. Also, knowledge of the mineral matter composition in a metallurgical coal and its transformation during the coking process is important for improving our interpretation of Coke Reactivity Index, CRI and Coke Strength after Reaction, CSR. As mineral matter is a minor component of coal, before it can be studied using conventional mineralogical techniques including quantitative X-ray diffraction, it needs to be concentrated by removing its organic content. This is effectively achieved using low temperature plasma ashing. This is accomplished by grinding the coal to a fine powder, (typically less than 212µm), then ashing using oxygen plasma followed by remixing the coal and further ashing until a constant weight is obtained. For trace elemental analysis the process is more involved and combines plasma ashing sample dissolution and analysis by methods such as ICP-AES or ICP-MS. We will present data showing reduction in organic sample weight of coal, coke and oil sand samples using low temperature (40 to 50^{o}C) plasma ashing. The majority of samples show that ashing time of 100 to 150 hours using 13.56MHz RF power at 100 Watts and 250 scc/min O_2 gas flow is sufficient to completely rid these of the organic/combustible matter.

INTRODUCTION
What is plasma?: Plasma is a state of matter just as a solid, liquid or gas. Add enough energy to a gas and it is partially ionized into the fourth state of matter – plasma (Figure 1). The free electrons present in the plasma can be accelerated by application of an electric field. Gases fed into the plasma are chemically activated through collisions with these fast moving electrons. The result is a highly chemically reactive environment that can be used to treat surfaces of materials. One important use of plasma is the low temperature combustion of organic matter from surfaces

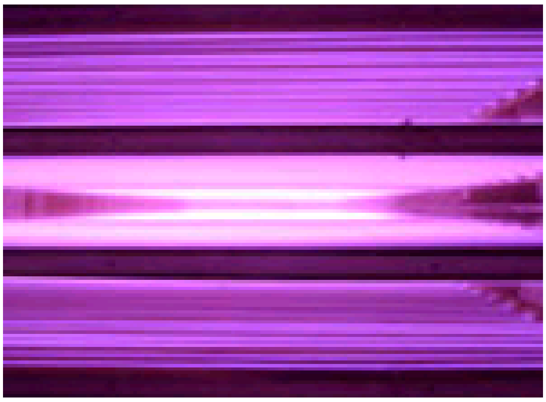

Fig 1. Plasma glow as viewed in a vacuum chamber

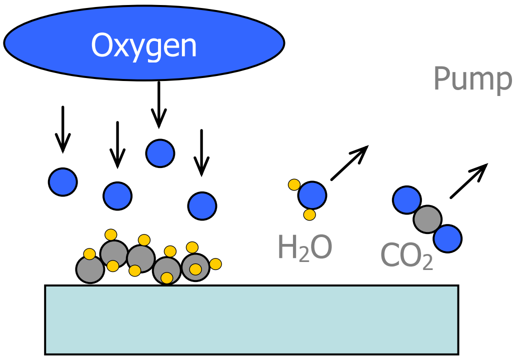

Fig 2 Molecular representation of plasma ashing

Plasma ashing: Oxygen plasmas are very effective at low temperature ashing of organic matter. The chemical pathway is a simple combustion process that converts hydrocarbons in the presence of activated oxygen to CO_2 and H_2O. The difference between plasma combustion and that normally associated with the burning of fossil fuels is temperature. The combustion process in a plasma is initiated by the high kinetic energy of the electrons whereas burning fuel is initiated by the Plasma ashes organic material by converting hydrocarbons to volatile gases that are removed by the pump, e.g.: CxHy (surface bound)+ O2 (plasma activated) → CO2 + H2O (Figure 2)

Ashing coal: Coal (Figure 3) can be ashed to isolate the mineral content prior to quantitative analysis using X-ray diffraction (XRD). XRD identifies minerals such as illite, gypsum, kaolimite, quartz, ankerite and pyrite. Quantification is possible providing all the organic content is removed. This achieved by grinding the coal to a fine powder, ashing oxygen plasma to constant weight, regrinding and ashing again to constant weight. For trace elemental analysis the process is more involved and combines plasma ashing with photoemission spectroscopy and mass spectrometry for real time analysis.

METHODS

The coal (oil sand) samples were ground to a fine powder less than 212µm using a pestle and mortar (Figure 3). 1g of each sample was dispersed over the surface of 6" diameter soda lime glass petri dishes. The coal samples were placed in the PVAtepla IoN40 system (Corona CA) (Figure 4) on one of 5 electrode trays. A vacuum was pulled down to 50mT. The oxygen gas flow into the chamber was set to 250 cc/min and the RF (13.56MHz) power was set to 100W. The sample temperature and in the plasma chamber temperature averaged 60C during the whole experiment. Every 24 hrs the samples were removed from the IoN40 plasma system and the coal powder was re-dispersed. The samples were weighed each 24hrs to track the loss of organic mass. This was continued until no more mass reduction was measured.

Fig3. Coal powder samples magnified 30 times

Fig4. IoN40 RF gas plasma system

RESULTS

Oil Sand LTA Samples									
Start_Sept 15 2011									
Tray Weight									
Time	Power	1	2	3	4	5	6	7	8
empty	100	19.0187	15.9451	17.0485	16.6380	16.4525	17.6979	17.2875	16.298
0	100	19.5207	16.4578	17.5586	17.1454	16.9616	18.2031	17.7938	16.8025
18	100	19.4900	16.4535	17.5558	17.1200	16.9433	18.1870	17.7765	16.7871
66	100	19.4935	16.4554	17.5578	17.1189	16.943	18.1869	17.7759	16.7868
90	100	19.4919	16.455	17.5578	17.1186	16.9428	18.1867	17.7762	16.7872
114	100	19.4967	16.4557	17.5585	17.1188	16.943	18.1868	17.7762	16.787
138	100	19.4967	16.4557	17.5585	17.1188	16.943	18.1868	17.7762	16.787
162	100	19.4967	16.4557	17.5585	17.1188	16.943	18.1868	17.7762	16.787
180	100	19.4967	16.4557	17.5585	17.1188	16.943	18.1868	17.7762	16.787
Coal weight									
Time	Power	1	2	3	4	5	6	7	8
empty	100								
0	100	0.502	0.5127	0.5101	0.5074	0.5091	0.5052	0.5063	0.5045
18	100	0.4713	0.5084	0.5073	0.482	0.4908	0.4891	0.489	0.4891
66	100	0.4748	0.5103	0.5093	0.4809	0.4905	0.489	0.4884	0.4888
90	100	0.4732	0.5099	0.5093	0.4806	0.4903	0.4888	0.4887	0.4892
114	100	0.478	0.5106	0.51	0.4808	0.4905	0.4889	0.4887	0.489
138	100	0.478	0.5106	0.51	0.4808	0.4905	0.4889	0.4887	0.489
162	100	0.478	0.5106	0.51	0.4808	0.4905	0.4889	0.4887	0.489
180	100	0.478	0.5106	0.51	0.4808	0.4905	0.4889	0.4887	0.489
Weight Percent									
Time	Power	1	2	3	4	5	6	7	8
empty	100								
0	100								
18	100	93.88	99.16	99.45	94.99	96.41	96.81	96.58	96.95

66	100	94.58	99.53	99.84	94.78	96.35	96.79	96.46	96.89
90	100	94.26	99.45	99.84	94.72	96.31	96.75	96.52	96.97
114	100	95.22	99.59	99.98	94.76	96.35	96.77	96.52	96.93
138	100	95.22	99.59	99.98	94.76	96.35	96.77	96.52	96.93
162	100	95.22	99.59	99.98	94.76	96.35	96.77	96.52	96.93
180	100	95.22	99.59	99.98	94.76	96.35	96.77	96.52	96.93

Tray Weight

Time	Power	12	13	14	15	16	17	18	19
empty	100	16.9895	17.3531	16.2510	16.7802	16.8183	16.9186	16.6179	17.6206
0	100	17.4963	17.8620	16.7556	17.2929	17.3274	17.4219	17.1229	18.1275
18	100	17.3757	17.7104	16.7533	17.2915	17.3067	17.4095	17.1114	18.1180
66	100	17.3407	17.6588	16.7538	17.2918	17.3058	17.4096	17.1113	18.1185
90	100	17.3333	17.6407	16.7537	17.2918	17.3065	17.4100	17.1120	18.1188
114	100	17.3175	17.6252	16.7537	17.2918	17.3045	17.4094	17.1108	18.1178
138	100	17.3068	17.6127	16.7537	17.2918	17.3024	17.4094	17.1108	18.1178
162	100	17.3000	17.6055	16.7537	17.2918	17.3027	17.4094	17.1108	18.1178
180	100	17.3098	17.6146	16.7537	17.2918	17.3027	17.4094	17.1108	18.1178

Coal weight

Time	Power	12	13	14	15	16	17	18	19
empty	100								
0	100	0.5068	0.5089	0.5046	0.5127	0.5091	0.5033	0.505	0.5069
18	100	0.3862	0.3573	0.5023	0.5113	0.4884	0.4909	0.4935	0.4974
66	100	0.3512	0.3057	0.5028	0.5116	0.4875	0.491	0.4934	0.4979
90	100	0.3438	0.2876	0.5027	0.5116	0.4882	0.4914	0.4941	0.4982
114	100	0.328	0.2721	0.5027	0.5116	0.4862	0.4908	0.4929	0.4972
138	100	0.3173	0.2596	0.5027	0.5116	0.4841	0.4908	0.4929	0.4972
162	100	0.3105	0.2524	0.5027	0.5116	0.4844	0.4908	0.4929	0.4972
180	100	0.3203	0.2615	0.5027	0.5116	0.4844	0.4908	0.4929	0.4972

Weight Percent

Time	Power	12	13	14	15	16	17	18	19
empty	100								
0	100								
18	100	76.20	70.21	99.54	99.73	95.93	97.54	97.72	98.13
66	100	69.30	60.07	99.64	99.79	95.76	97.56	97.70	98.22
90	100	67.84	56.51	99.62	99.79	95.89	97.64	97.84	98.28
114	100	64.72	53.47	99.62	99.79	95.50	97.52	97.60	98.09
138	100	62.61	51.01	99.62	99.79	95.09	97.52	97.60	98.09
162	100	61.27	49.60	99.62	99.79	95.15	97.52	97.60	98.09
180	100	63.20	51.39	99.62	99.79	95.15	97.52	97.60	98.09

Tray Weight

Time	Power	23	24	25	26	27	28	29	30
empty	100	17.2275	16.3141	16.8609	14.8129	17.1029	17.6377	17.0675	16.2444
0	100	17.7309	16.8206	17.3709	15.3252	17.6058	18.1439	17.5771	16.7523
18	100	17.7215	16.7979	17.3504	15.2942	17.5329	17.9802	17.5703	16.7343
66	100	17.7220	16.7970	17.3497	15.2921	17.5262	17.9579	17.5703	16.7334
90	100	17.7218	16.7969	17.3502	15.2925	17.5263	17.9545	17.5705	16.7332
114	100	17.7214	16.7947	17.3493	15.2905	17.5202	17.9455	17.5702	16.7320
138	100	17.7214	16.7940	17.3493	15.2888	17.5160	17.9395	17.5702	16.7314
162	100	17.7214	16.7940	17.3493	15.2883	17.5144	17.9348	17.5702	16.7314
180	100	17.7214	16.7940	17.3493	15.2898	17.5162	17.9364	17.5702	16.7314

Coal weight

Time	Power	23	24	25	26	27	28	29	30
empty	100								
0	100	0.5034	0.5065	0.51	0.5123	0.5029	0.5062	0.5096	0.5079
18	100	0.494	0.4838	0.4895	0.4813	0.43	0.3425	0.5028	0.4899
66	100	0.4945	0.4829	0.4888	0.4792	0.4233	0.3202	0.5028	0.489
90	100	0.4943	0.4828	0.4893	0.4796	0.4234	0.3168	0.503	0.4888
114	100	0.4939	0.4806	0.4884	0.4776	0.4173	0.3078	0.5027	0.4876
138	100	0.4939	0.4799	0.4884	0.4759	0.4131	0.3018	0.5027	0.487
162	100	0.4939	0.4799	0.4884	0.4754	0.4115	0.2971	0.5027	0.487
180	100	0.4939	0.4799	0.4884	0.4769	0.4133	0.2987	0.5027	0.487

Weight Percent

Time	Power	23	24	25	26	27	28	29	30
empty	100								
0	100								
18	100	98.13	95.52	95.98	93.95	85.50	67.66	98.67	96.46
66	100	98.23	95.34	95.84	93.54	84.17	63.26	98.67	96.28
90	100	98.19	95.32	95.94	93.62	84.19	62.58	98.70	96.24
114	100	98.11	94.89	95.76	93.23	82.98	60.81	98.65	96.00
138	100	98.11	94.75	95.76	92.89	82.14	59.62	98.65	95.89
162	100	98.11	94.75	95.76	92.80	81.83	58.69	98.65	95.89
180	100	98.11	94.75	95.76	93.09	82.18	59.01	98.65	95.89

Tray Weight

Time	Power	34	35	36	37	38	39	40
empty	100	17.1055	15.7133	16.7589	16.3904	16.6351	16.4923	16.8273
0	100	17.6079	16.2256	17.2660	16.8937	17.1387	17.0041	17.3361
18	100	17.5992	16.2188	17.2577	16.8822	17.1273	16.9933	17.3263
66	100	17.5988	16.2186	17.2573	16.8815	17.1266	16.9927	17.3258

90	100	17.5989	16.2187	17.2576	16.8819	17.1269	16.9931	17.3261
114	100	17.5986	16.2180	17.2569	16.8807	17.1261	16.9920	17.3257
138	100	17.5986	16.2179	17.2565	16.8802	17.1259	16.9915	17.3257
162	100	17.5986	16.2179	17.2567	16.8802	17.1257	16.9917	17.3257
180	100	17.5986	16.2179	17.2567	16.8802	17.1257	16.9917	17.3257
Coal weight								
Time	Power	34	35	36	37	38	39	40
empty	100							
0	100	0.5024	0.5123	0.5071	0.5033	0.5036	0.5118	0.5088
18	100	0.4937	0.5055	0.4988	0.4918	0.4922	0.501	0.499
66	100	0.4933	0.5053	0.4984	0.4911	0.4915	0.5004	0.4985
90	100	0.4934	0.5054	0.4987	0.4915	0.4918	0.5008	0.4988
114	100	0.4931	0.5047	0.498	0.4903	0.491	0.4997	0.4984
138	100	0.4931	0.5046	0.4976	0.4898	0.4908	0.4992	0.4984
162	100	0.4931	0.5046	0.4978	0.4898	0.4906	0.4994	0.4984
180	100	0.4931	0.5046	0.4978	0.4898	0.4906	0.4994	0.4984
Weight Percent								
Time	Power	34	35	36	37	38	39	40
empty	100							
0	100							
18	100	98.27	98.67	98.36	97.72	97.74	97.89	98.07
66	100	98.19	98.63	98.28	97.58	97.60	97.77	97.98
90	100	98.21	98.65	98.34	97.66	97.66	97.85	98.03
114	100	98.15	98.52	98.21	97.42	97.50	97.64	97.96
138	100	98.15	98.50	98.13	97.32	97.46	97.54	97.96
162	100	98.15	98.50	98.17	97.32	97.42	97.58	97.96
180	100	98.15	98.50	98.17	97.32	97.42	97.58	97.96

CONCLUSIONS

The majority of samples show that ashing time of 100 to 150 hours using 13.56MHz RF in the IoN40 system with power set at 100 Watts and 250 scc/min O_2 gas flow is sufficient to completely rid these of the organic/combustible matter (Table1). We were able to present data showing the reduction in organic sample weight of coal, coke and oil sand samples using low temperature (40 to 50^{o}C) plasma ashing. For trace elemental analysis the process was more involved and combines plasma ashing sample dissolution and analysis by methods such as ICP-AES or ICP-MS.

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