Qualitative and Quantity analysis of scale samples from cracking gas compressors

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Abstract: This paper explores the joint use of qualitative and semi-quantitative equipment such as C, H, N element analyzers, x-fluorescence spectrometers, Inductively coupled plasma atomic emission spectrometers (ICP) and gas chromatography-mass spectrometry (gc-ms), the scale sample of cracking gas compressor was analyzed qualitatively and comprehensively. C and H (91.77%) are the main elements in the scale sample of the first stage outlet pipeline of cracking gas compressor, the scaling may be caused by the polymerization of unsaturated hydrocarbons and the coking of macromolecular aromatics. The scale sample of the heat exchanger contains a large amount of inorganic components and the ash content reaches 52.51%, there are also deposits of sodium salts, silicates and sulphates to form scale.

Keywords: Scale sample; C, H, N Element Analyzer; X-fluorescence spectrometer; Inductively coupled plasma atomic emission spectroscopy; Industrial analysis; Sulfur content

1 Introduce

Scale is a deposit that forms on heating surfaces and heat transfer surfaces, generated by precipitation or certain actions from water or other media. Accurate analysis of scale samples can provide a basis for maintenance decisions and enable production managers to take timely preventive measures or remedial actions, thus avoiding re-scaling in systems after major overhauls. Therefore, scale sample analysis is of great significance for equipment maintenance and operation management[1-2].

Compressors are the core large-scale equipment in naphtha cracking units, and their "safe, stable, long-term, full, and optimal" operation is crucial. A company's cracking unit experienced fluctuations in the inlet pressure of the first stage of the cracked gas compressor and increased abnormal noise. It was discovered that there was a large amount of coke and scale in the outlet pipeline and the outlet heat exchanger of the first stage of the cracked gas compressor, causing unstable operation of the compressor. As the coking problem worsened, the unit was forced to shut down for maintenance[3].

For the analysis of scale samples, only comprehensive and accurate qualitative analysis can lead to better quantitative analysis, which can truly guide the production to analyze the causes of the structure and take appropriate measures. The chemical titration method in HG/T 3534 "Methods for Determination of Acid-Insoluble Substances, Phosphorus, Iron, Aluminum, Calcium, Magnesium, Zinc, and Copper Content in Industrial Circulating Cooling Water Scale and Corrosion Products" has issues with the titration endpoint not being distinct and large errors in measurement results when analyzing elements such as phosphorus, iron, aluminum, calcium, magnesium, zinc, and copper[4-5]. This paper explores the combined use of elemental analyzers, X-ray fluorescence spectrometers, inductively coupled plasma atomic emission spectroscopy (ICP), and gas chromatography-mass spectrometry (GC-MS), which have qualitative and semi-quantitative functions, for the analysis of scale samples from the cracked gas compressor.

2 Experimental Section

2.1 Instruments and Reagents

- Industrial analyzer
- CHN elemental analyzer
- X-ray fluorescence spectrometer (XRF)
- Inductively coupled plasma atomic emission spectrometer (ICP-AES)
- Gas chromatography-mass spectrometer (GC-MS)

2.2 Experimental Methods

For the analysis of scale samples, comprehensive and accurate qualitative analysis is essential for better

quantitative analysis. Based on the principles of industrial analysis and sulfur content analysis of coal, instruments such as the elemental analyzer, X-ray fluorescence spectrometer, inductively coupled plasma atomic emission spectrometer (ICP), and gas chromatography-mass spectrometer (GC-MS), which possess qualitative and semi-quantitative capabilities, are used for combined analysis to determine the causes of scaling.

The CHN elemental analyzer works by oxidizing the sample at high temperatures in the presence of a composite catalyst, producing nitrogen gas, nitrogen oxides, carbon dioxide, sulfur dioxide, and water. These products are then carried into the separation and detection unit by a carrier gas. Compounds of non-nitrogen elements are retained in an adsorption column, while nitrogen oxides are reduced to nitrogen gas and detected. The oxides of other elements are separated and analyzed sequentially by an adsorption-desorption column, determining the elements C, H, and S.

X-ray fluorescence (XRF) occurs when primary X-rays irradiate a sample, causing the inner shell electrons of stimulated atoms to produce characteristic secondary X-rays through energy level transitions. The energy and intensity of these secondary X-rays can be detected and are related to the content of the elements within the sample.

Inductively coupled plasma (ICP) can reach temperatures of 6000-8000 K. When a sample is introduced into the nebulizer via an injector and carried into the plasma by argon gas, its components are atomized, ionized, and excited, emitting energy in the form of light. Different elements emit characteristic spectra at specific wavelengths when returning to their ground state from an excited or ionized state. Therefore, qualitative analysis can be conducted based on the wavelengths of the characteristic light, while quantitative analysis can be performed based on the intensity of the emitted light corresponding to different element concentrations.

A gas chromatography-mass spectrometer (GC-MS) combines the capabilities of gas chromatography and mass spectrometry. Chromatography is an effective method for separating organic compounds, while mass spectrometry can perform accurate qualitative analysis. The effective combination of these two techniques provides chemists and biochemists with a powerful tool for the efficient qualitative and quantitative analysis of complex organic compounds[6].

3 Results and Discussion

3.1 Ash and ash composition analysis

3.1.1 Ash analysis

Ash analysis with reference to GB/T 212-2008 "coal industrial analysis methods" [7], the scale sample grinding, mixing, weighing 1 g sample, calcined at 500 ℃ for 30 min, 815 ℃ calcined for 1 h, the state of the calcined state is shown in Figure 1.

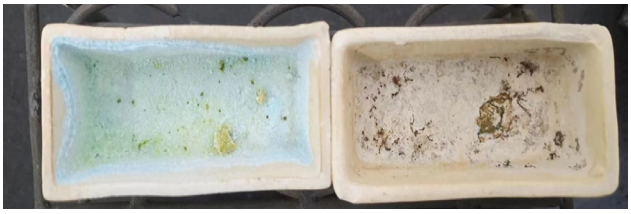

Figure 1 Cracked gas compressor section outlet line fouling samples after calcination; Cracked gas compressor section outlet heat exchanger after calcination of scale samples

Cracked gas compressor outlet line scale sample calcined with a small amount of blackish gray ash residue and adhering to the dry pan wall, hard texture, ash content 1.64 %. The heat exchanger scale sample at the outlet of the cracked gas compressor has a large amount of blue semi-crystalline material remaining and adhering to the wall of the dry pot, with a hard texture and an ash content of 52.51 %. The results are shown in Table 1.

Table 1 Ash analysis results of scale samples

No	Sample Name	Ash % (m/m)	Condition
1	Fouling of a section of the cracked gas compressor outlet line	1.64	Dark gray, hard texture
2	Cracked gas compressor section outlet heat exchanger scale sample	52.51	Blue semi-crystalline, hard texture

3.1.2 Analysis of ash elemental composition

X-fluorescence spectrometer was used to analyze the composition of ash [8-9], cracked gas compressor one

section of the exit pipeline scale sample ash can not melt the flake, can not be analyzed; cracked gas compressor one section of the exit heat exchanger scale samples in the ash is mainly composed of sodium, silicon, sulfur, and contains a small amount of iron, calcium, magnesium, potassium, and other elements, the results of the analysis are shown in Table 2.

Table 2 Elemental analysis results in ash

No	Sample Name	Ash fraction (X-fluorescence) %								
		SiO_2	Al_2O_3	$Fe2O_3$	CaO	MgO	TiO	K2O	Na_2O	SO_3
	Cracked gas compressor section outlet heat exchanger scale sample	12.39	1.64	0.55	0.32	0.325	0.09	0.58	45.68	11.2

3.2 Elemental analysis in scale samples

3.2.1 Elemental analysis of C, H and N in scale samples

The elemental analyzer is used to analyze the carbon, hydrogen and nitrogen elements in the scale samples, in which the total content of carbon, hydrogen and nitrogen elements in the compressor outlet scale samples is 91.82%, and the total content of carbon, hydrogen and nitrogen elements in the heat exchanger scale samples is 59.06%, so it can be seen that the two kinds of scale samples contain a large number of organic hydrocarbons, and the specific analysis results are shown in Table 3.

Table 3 C, H and N content in scale samples

No	Sample Name	Elemental content of hydrocarbon and nitrogen (elemental analyzer) / %			
		C	H	N	Other (shortfall)
1	Fouling of a section of the cracked gas compressor outlet line	83.21	8.56	0.05	8.18
2	Cracked gas compressor section outlet heat exchanger scale sample	53.05	5.82	0.19	40.94

3.2.2 Elemental analysis in scale samples-ICP method

After grinding the scale sample, weigh 0.5 g of sample to the porcelain crucible, ashing at 450℃ for 30 min, respectively, add 30 mL of concentrated hydrochloric acid, 10 mL of concentrated nitric acid, heated to translucent, add 20 mL of perchloric acid heating to smoke, cooled by adding 50 mL of demineralized water to dissolve the filtration, which intercepted in the filter paper insoluble in the filter paper at 950℃ after 1 h constant weight, weighing, analysis of acid insoluble material (mainly composed of SiO_2), the solution using ICP to determine the elemental content [10-12]. component is SiO_2), and the solution was determined by ICP for elemental content. In addition to carbon and hydrogen elements, the main elements in the compressor outlet scale samples are sodium, silicon and iron, and the main elements in the heat exchanger scale samples are sodium and silicon. The specific measurement results are shown in Table 4.

Table 4 ICP results of fouling samples

No	Sample Name	Acid insoluble matter (SiO_2)/ %	Elemental analysis (ICP method)			
			Na %	K %	Fe %	Mg %
1	Fouling of a section of the cracked gas compressor outlet line	0.31	0.45	0.01	0.11	/
2	Cracked gas compressor section outlet heat exchanger scale sample	1.85	6.82	0.24	0.16	0.04

3.2.3 Elemental analysis in scale samples

After grinding the scale samples, X-fluorescence was used directly for qualitative and semi-quantitative analysis. The main elements in the scale samples of one section of the outlet pipeline of the cracked gas compressor were sulfur, iron, phosphorus, calcium, silicon and potassium; the main elements in the scale samples of one section of the heat exchanger of the outlet of the cracked gas compressor were sodium, sulfur, phosphorus, calcium, silicon and potassium, and the main elements were in agreement with the results of the determination of the ash fraction by the ICP and X-fluorescence methods. The specific analysis results are shown in Table 5.

Table 5 Results of X-fluorescence determination of fouling samples

No	Sample Name	Elemental semi-quantitative analysis (X-fluorescence) %									
		Na	S	Fe	P	K	Ca	Si	Cl	Pb	Pd
1	Fouling of a section of the cracked gas compressor outlet line	/	0.56	0.08	0.08	0.04	0.04	0.01	0.01	/	0.004
2	Cracked gas compressor section outlet heat exchanger scale sample	13.5	9.94	0.1	0.2	0.02	0.17	0.06	/	0.02	/

3.2.4 Analysis of CS2 leachate content-GC-MS method

The milled scale samples were added to the CS_2 solvent for dissolution and filtered, and the CS_2 dissolved matter was qualitatively analyzed by GC-MS [13-14] to determine the type of organic matter. The specific test results are shown in Table 6 and Table 7, respectively.

Table 6 Temperature semi-quantitative results of CS_2 dissolved matter in a section of the cracked gas compressor outlet line scale sample

No	Molecular formula	Similarity	Percentage of area (excluding CS_2)
1	C8H8	97	21.86
2	C9H8	94	12.22
3	C7H8	97	10.46
4	C6H6	98	9.98
5	C8H10	98	3.81
6	C18H34O2	95	3.75
7	C9H10	97	3.75
8	C9H10	97	2.24
9	C16H34	97	2.02
10	C13H14	92	2.01
11	C8H18	93	1.95
12	C8H10	98	1.762
13	C10H12	97	1.77
14	C19H40	97	1.76
15	C9H20	95	1.47
16	C7H16	97	1.08

Table 7 Gas chromatography semi-quantitative results of CS2 dissolved matter in a heat exchanger scale sample at the outlet of a cracked gas compressor section

No	Molecular formula	Similarity	Percentage of area (excluding CS_2)
1	H2S	95	72.34
2	C8H8	95	5.29
3	C6H6	98	4.56
4	C9H8	94	4.48
5	C7H8	97	3.25
6	C8H10	96	1.46

3.2.5 Determination of sulfur content

The determination of sulfur content refers to GB/T 214-2007 "Method for Determination of Total Sulfur in Coal" [15], the two scale samples contain sulfur, in which the sulfur content in the heat exchanger scale samples is as high as 11.72%, and the analytical results are consistent with the results of the X-fluorescence method. Specific analysis results are shown in Table 8.

Table 8 Analytical results of sulfur content scale samples

No	Sample Name	Sulfur content % (m/m)
1	Fouling of a section of the cracked gas compressor outlet line	0.78
2	Cracked gas compressor section outlet heat exchanger scale sample	11.72

4 Conclusion

Through combined testing using instruments with qualitative and semi-quantitative capabilities such as the elemental analyzer, X-ray fluorescence spectrometer (XRF), inductively coupled plasma atomic emission spectrometer (ICP), gas chromatography-mass spectrometer (GC-MS), and infrared spectrometer, the following conclusions can be drawn:

1. The main elements in the scale sample from the first-stage outlet pipeline of the cracked gas compressor are carbon and hydrogen (accounting for 91.77%). The primary components are aromatic compounds and polymers of unsaturated hydrocarbons. Additionally, there are elements such as sulfur (approximately 0.78%), iron (approximately 0.1%), and phosphorus (approximately 0.08%). The scaling is likely due to the polymerization of unsaturated hydrocarbons and the formation of coke from large aromatic molecules in the cracked products.

2. The scale sample from the first-stage outlet heat exchanger of the cracked gas compressor contains a significant amount of inorganic components, with an ash content of 52.51%. Besides carbon and hydrogen, it contains substantial amounts of sodium (approximately 13.50%), sulfur (approximately 11.72%), and silicon (approximately 1.85%). This indicates that, in addition to coke formation from the polymerization of unsaturated hydrocarbons and large aromatic molecules, the scaling also includes deposits formed from sodium salts, silicates, and sulfates.

3. Both scale samples contain a considerable amount of sulfur, especially the sample from the first-stage outlet heat exchanger of the compressor, where the sulfur content reaches 11.72%. Even after high-temperature combustion at 815°C, 11.2% of sulfur was still detected in the ash. This suggests that sulfur in the heat exchanger

scale sample primarily exists in the form of sulfates. Since the cracked feedstock (naphtha, LPG) does not contain sulfur, it is inferred that the sulfur mainly originates from the cracking additive dimethyl disulfide.

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