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Chromium-6 analysis of converter and cast house slag

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1 SUMMARY

Nebest B.V. received three samples of blast furnace slag from Tata Steel:

MM1-B Converter slag Class 2
MM2-B Converter slag Class 3
MM3-B Cast house slag

Nebest is asked to determine if there is chromium-6 (Cr^{6+}) present in the slag.

The following examinations are performed on sample MM1-B and sample MM3-B:

- Sample preparation:
  - Homogenizing
  - Crushing
  - Take three subsamples per sample
  - Homogenizing of subsample
- XRF analysis of subsamples
- Indication test to determine presence of chromium-6 qualitatively
- Chemical analysis to determine presence of chromium-6 quantitatively
- Chemical analysis to determine presence of total chromium quantitatively
- EDX analysis of subsamples

The analyses show that chromium is present in both samples. The chromium content in sample MM1-B is 1487 mg/kg and in sample MM3-B 292 mg/kg. Chromium-6 could not be detected in the samples.

2 EXAMINATION

The samples as received are shown in Figure 1 to Figure 6. Only sample MM1-B and MM3-B are analyzed at the request of the client. Before analysis of the samples, these are crushed. From the crushed samples three subsamples are taken. These subsamples are homogenized in order to obtain a fine powder.

From sample MM1-B subsamples 1.1, 1.2 and 1.3 are obtained, whereas from sample MM3-B subsamples 3.1, 3.2 and 3.3 are obtained.

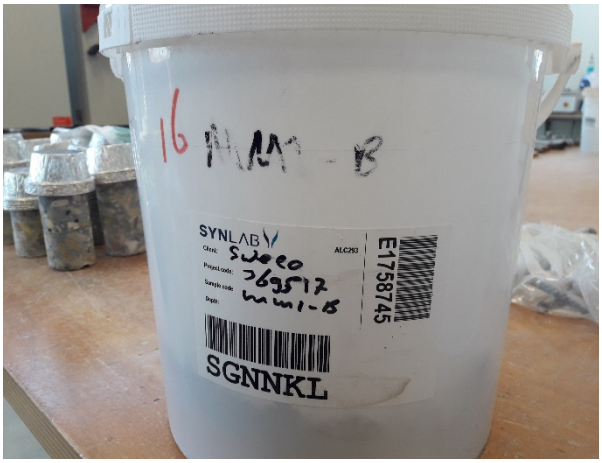

Figure 1: Sample MM1-B.

Figure 2: Sample MM1-B

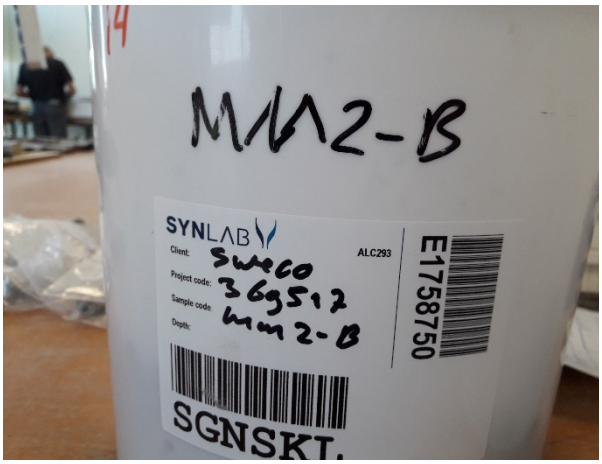

Figure 3: Sample MM2-B

Figure 4: Sample MM2-B

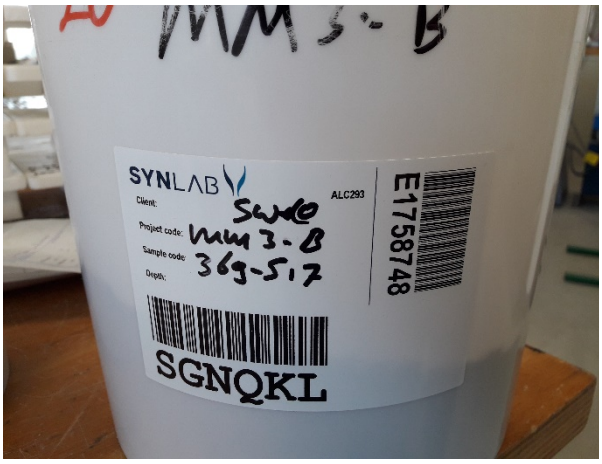

Figure 5: Sample MM3-B

Figure 6: Sample MM3-B

2.1 XRF analysis

The six subsamples are analyzed with an X-ray fluorescent (XRF) analyzer to determine the presence of chromium. Only if chromium is present, chromium-6 can be present in the sample. Apart from chromium also the presence of aluminum, copper, iron, nickel and zinc is determined. These so-called analysis-disturbing elements could play a role in the determination of the chromium-6 content. During chemical analyses these elements can either cause reduction of chromium-6 towards chromium-3, or form a complex with the chromium-6 indicator. In both cases this hinders the determination and quantification of chromium-6. The results of the XRF analyses are given in Table 1.

Table 1: Presence of chromium and analysis-disturbing elements in subsamples as determined with XRF.

Sample	Al	Cr	Cu	Fe	Ni	Zn
1.1	+	+++	-	+++	-	+
1.2	+	+++	-	+++	-	+
1.3	+	+++	-	+++	-	+
3.1	+++	+	-	++	-	+
3.2	+++	+	-	++	-	+
3.3	+++	+	-	++	-	+

2.2 Chromium-6 indication test

On the six subsamples a chromium-6 indication test is performed. For this test a small amount of sample is placed in an analysis tube. An acidic solution is added to the sample, followed by a solution of a chromium-6 indicator. The chromium-6 indicator used is 1,5 diphenyl carbazide. If chromium-6 leaches from the sample in the solution, it forms a complex with the indicator. This complex has a purple color. A purple discoloration therefore indicates the presence of chromium-6. When no discoloration is seen, however, chromium-6 can still be present in the sample, but might not leach into the solution. The results of the chromium-6 indication tests are given in Table 2.

Table 2: Results of chromium-6 indication test.

Sample	1.1	1.2	1.3	3.1	3.2	3.3
Chromium-6 presence	Not found	Not found	Not found	Not found	Not found	Not found

2.3 Chemical analysis for chromium-6 detection

On all six subsamples a chemical analysis is performed. For this analysis a small amount of sample is heated in an alkaline extraction solution for a certain amount of time to extract the chromium-6 from the sample. The sample is then let to cool down to room temperature. A small amount of the extraction solution is then mixed with an acidic solution and a solution with the chromium-6 indicator.
If chromium-6 is present in the extraction solution, it will react with the indicator and lead to a purple discoloration of the fluid. With a UV/Vis spectrometer the absorbance of light at the specific wave-length of the chromium-6 indicator complex is determined. This absorbance is a measure for the amount of chromium-6 extracted from the sample.

For the three subsamples per sample the extraction time is varied to determine its influence on the results. A longer extraction time could lead to more chromium-6 being extracted from the sample and with that increase the extraction efficiency. However, since during a longer extraction also more analysis-disturbing elements could be extracted from the sample, this could also lead to reduction of chromium-6 towards chromium-3. In this case a longer extraction will lead to a lower amount of chromium-6 found.

For all subsamples a second analysis is performed with a known amount of chromium-6 added to the sample, a so-called spike. If the chromium-6 is stable during the extraction, 100% of the spike will be recovered. However, if reduction of chromium-6 towards chromium-3 occurs during the extraction due to the presence of analysis-disturbing elements, only a smaller amount of the spike will be recovered. The amount of spike recovery is therefore a measure of the reliability of the analysis result.

The results of the chemical analysis are given in Table 3. From the spike recovery being significantly lower than 100% it can be concluded that chromium-6 from the spike is reduced to chromium-3 during the extraction. If chromium-6 is extracted from the sample this will also be reduced. It is well possible that all chromium-6 extracted from the sample is reduced, resulting in no chromium-6 detection.

Table 3: Results of chemical analysis for chromium-6 detection as determined with UV/Vis spectrometer.

Sample	**Extraction duration [min]**	**Chromium-6 [mg/kg]**	**Spike recovery [%]**
1.1	20	Not found	40
1.2	60	Not found	61
1.3	120	Not found	54
3.1	20	Not found	40
3.2	60	Not found	48
3.3	120	Not found	46

2.4 Chemical analysis for chromium detection

Although the XRF measurements already showed the presence of chromium, the exact amount can be more reliably determined with a chemical analysis. For this a small amount of sample is heated in an acidic extraction solution. During extraction all chromium present is extracted from the sample. After cooling down the extraction solution is analyzed with atomic absorption spectroscopy (AAS) to measure the concentration of chromium in the fluid.

Table 4: Results of chemical analysis for chromium detection as determined with AAS.

Sample	Chromium [mg/kg]
MM1-B	1487
MM3-B	292

2.5 SEM/EDX analysis

All subsamples are analyzed with the scanning electron microscope (SEM) and the energy-dispersive X-ray spectroscopy detector (EDX). SEM images of subsamples 1.3 and 3.3 are shown in Figure 7 and Figure 8. The EDX spectra determined of these samples are shown in Figure 9 and Figure 10. The chemical composition of the samples is given in Table 5.

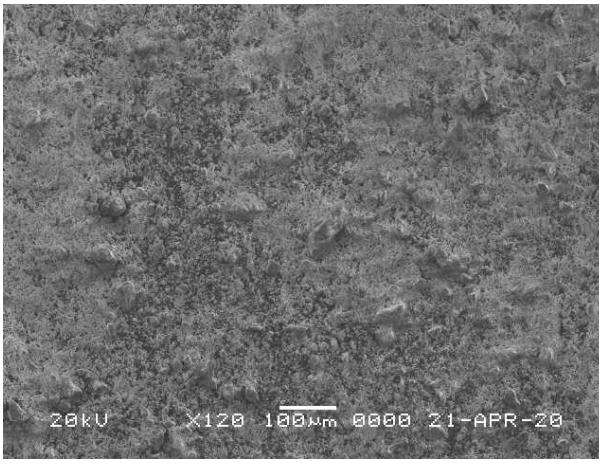

Figure 7: SEM image of sample 1.3.

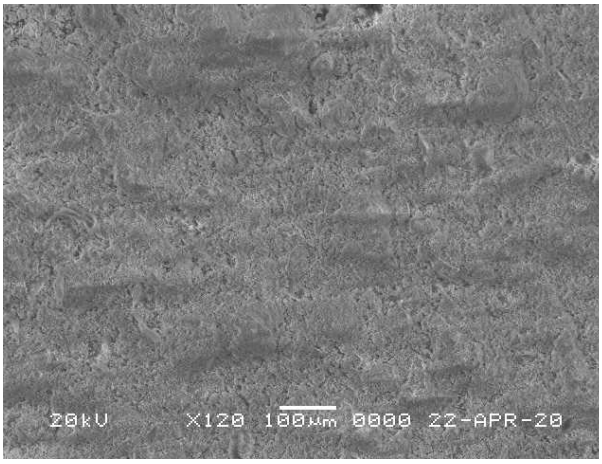

Figure 8: SEM image of sample 3.3.

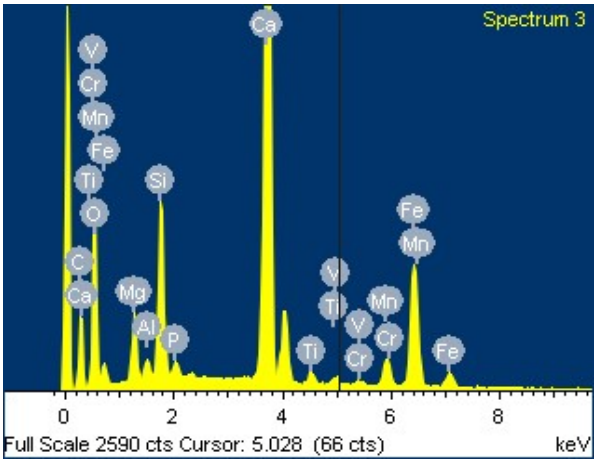

Figure 9: EDX spectrum of sample 1.3.

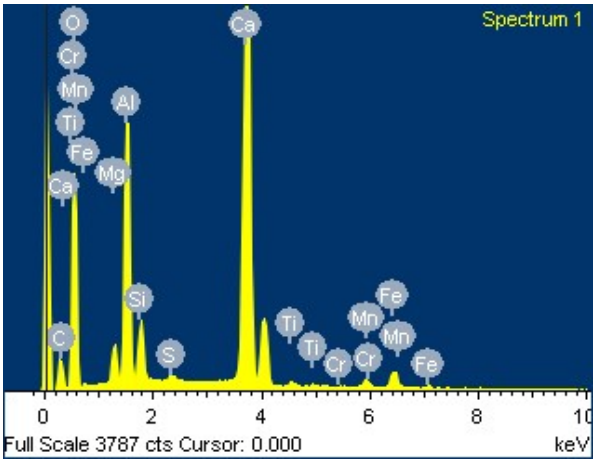

Figure 10: EDX spectrum of sample 3.3

Table 5: Results of semi-quantitative analysis of chemical composition of samples with EDX. All results are in weight percent.

Sample	%C	%O	%Mg	%Al	%Si	%P	%S	%Ca	%Ti	%V	%Cr	%Mn	%Fe
1.1	15	37	2.5	0.72	5.1	0.42		24	0.69	0.53	0.26	2.5	13
1.2	19	36	2.6	0.80	4.5	0.38		21	0.63	0.49	0.18	2.5	12
1.3	15	37	2.6	0.60	5.0	0.52		23	0.80	0.41	0.22	2.6	13
3.1	12	46	1.9	8.9	2.4		0.20	25	0.23		0.08	1.2	2.7
3.2	21	44	1.6	7.6	2.0		0.29	20	0.28		0.16	0.82	2.0
3.3	13	49	1.6	8.7	2.3		0.28	22	0.24		0.15	0.90	2.0

3 DISCUSSION

The results of the examinations show that chromium is present in both samples. No chromium-6 is detected with the chromium-6 indication test or the chemical analysis. This can have three possible causes:

1. No chromium-6 is present in the samples.
2. No or too little chromium-6 is extracted from the slag.
3. Extracted chromium-6 is reduced towards chromium-3 as a result of oxidation of analysis-disturbing elements.

Causes 2 and 3 can occur simultaneously.

For both tests chromium-6 has to be extracted from the slag after which it can form a complex with the indicator 1,5 diphenyl carbazide.

For the chromium-6 indication test to function, chromium-6 has to leach out of the slag into the test fluid and then immediately form a complex with the indicator. This test is developed for chromium-6 detection in coatings. For coatings it is known that the degree of leaching of chromium-6 into the fluid is matrix dependent. For slag it is not known whether chromium-6 present will readily leach into the fluid.

For the chemical analysis to function, chromium-6 has to be extracted from the slag into the extraction fluid. The extraction parameters are optimized for chromium-6 detection in coatings. It is known that the time needed for 100% extraction of chromium-6 from coatings is matrix dependent. At the same time it is known that longer extraction times can lead to more extraction of other elements from the coating, which, dependent on the element, will oxidize with a chromium-6 towards chromium-3 reduction as a result.

Dependent on both the matrix as well as the concentration of chromium-6 and analysis-disturbing elements it is therefore possible that no chromium-6 is detected even though it is present in the sample. For the analysis of slag the same problems are expected.

Even though no chromium-6 is found, it cannot be ruled out that it is present in the slag. Since less than 100% of the spike is recovered in the analysis, it can be concluded that chromium-6 from the spike is reduced towards chromium-3. If chromium-6 has been extracted from the slag, this could also be reduced towards chromium-3. However, it is not known whether chromium-6 is extracted from the slag, or if it was not present in the slag at all.

4 CONCLUSION

From the results of the analyses of samples MM1-B and MM3-B the following conclusions can be drawn:

- Chromium is present in both analyzed samples.
- In both samples analysis-disturbing elements are present, leading to a reduction of chromium-6 from an added spike towards chromium-3 during the analysis.
- No chromium-6 is detected in the samples with the chromium-6 indication test or the chemical analysis.