ESTIMATION OF SLAG IN FERROCHROMIUM

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Introduction

The manufacture of Ferro Chromium involves the smelting of various ores and fluxes to produce the metallic product.

Slag is inherent in the process. It has a much lower density than the metallic FeCr. Some chrome may be trapped in the slag as either FeCr or Cr2O3.

Previous methods to estimate the slag in the FeCr have revolved around separating the slag and metallic portions by exploiting the differences in density. The downside with that procedure is that material will often contain pieces that are adhered FeCr and slag. The Metallic FeCr may also be completely encapsulated in the slag.

An alternative and more precise method involves calculating the slag content based on chemical analysis of Mg and Al. The Mg and Al will be at relatively low levels (less than 0.1%) in the Metallic FeCr pieces and considerably higher in the slag (3% or greater). The overall sample will have a proportional amount and is calculated using simultaneous equations with the assumption there is only one kind of slag and one kind of FeCr present. “Pure” slag and “pure” FeCr metal are needed in order to determine the Mg and Al in each. The determination of the Mg and Al in the overall sample would then be used to calculate the amount of slag.

When the particle size is small, it is difficult to sample and get “pure” pieces of the slag and FeCr metal of sufficient quantity to perform a proper analysis. Often, historic data is used but that is dependent on the source of the FeCr and the materials used in its production. Mg and Al levels in slag can vary between 3% and 20% in different FeCr slags depending on their origin.

Furnace Determination

The method uses an induction furnace with a graphite crucible to melt a dried sample of the FeCr fines. The material melts readily without additions. The slag rises to the top and the Metallic FeCr goes to the bottom of the crucible due to the density difference of each. The slag and metallic FeCr are collected, weighed, and compared to the input weight of the sample for recoveries of the slag and determination of loss. The Cr, Mg and Al in the overall sample are determined as well as in the Metallic FeCr and the slag from the melt through normal methods.

During the melting process some of the FeCr may become suspended in the slag. Assuming it is metallic ferrochrome, it adds undue weight to the slag. This must be accounted for in the

calculations. The Cr that is determined in metallic FeCr is the base value of the FeCr in the process. The amount of Cr in the slag is considered to be Metallic and suspended in the slag. Using the value for the metallic FeCr, an adjustment is made to the slag percentage by subtracting the amount of FeCr from the total weight.

A check of the process is the multiplication of the % of Cr in the original sample times the weight in grams. The amounts from the two melts are then subtracted.

Calculations

Using Mg and Al Results

The Mg and Al that are determined in the slag, overall sample and the Metallic FeCr are used to determine the amount of slag in the ferrochrome by simultaneous equations (see Excel spreadsheet). The concentration of Mg and Al in the slag is much higher than in the metallic material. The overall sample has values inbetween the other two indicating the percentage of slag.

Using Melt Data

The total weight of material put into the furnace is recorded to the nearest tenth of a gram. When the melt is complete, the slag is collected and weighed to the nearest tenth of a gram. After cooling, the metallic portion is weighed to the nearest tenth of a gram. The percent metallic recovery is calculated by dividing the weight of the metallic portion by the weight of material put into the furnace. The percent slag recovery is calculated along the same procedure. It is very probable that when the percent metallic recovery is added to the percent slag recovery it will total over 100%. This is due to the material picking up carbon from the graphite crucible during the process. A deduction is made to the amount of slag recovered based on the ferrochrome content after the chrome content of the slag is analyzed. The values of magnesium and aluminum are also adjusted.

Using Total Cr Results

The final look at the slag question involves the determination of the Cr in the melted ferrochrome sample and the amount of Cr determined in the Overall sample. If the metallic Cr is 50% and the overall sample is 48%, the difference is 2 %. Something must be present to dilute the value of the Cr. The approximate value of the good metal in the overall sample is 48%/50% or 96%. The amount of slag is then in the range of 4% (100%-96%). Analytical error for Chrome according to ISO 4552 is +/- 0.75%. This method for slag estimation has the greatest amount of error associated with it.

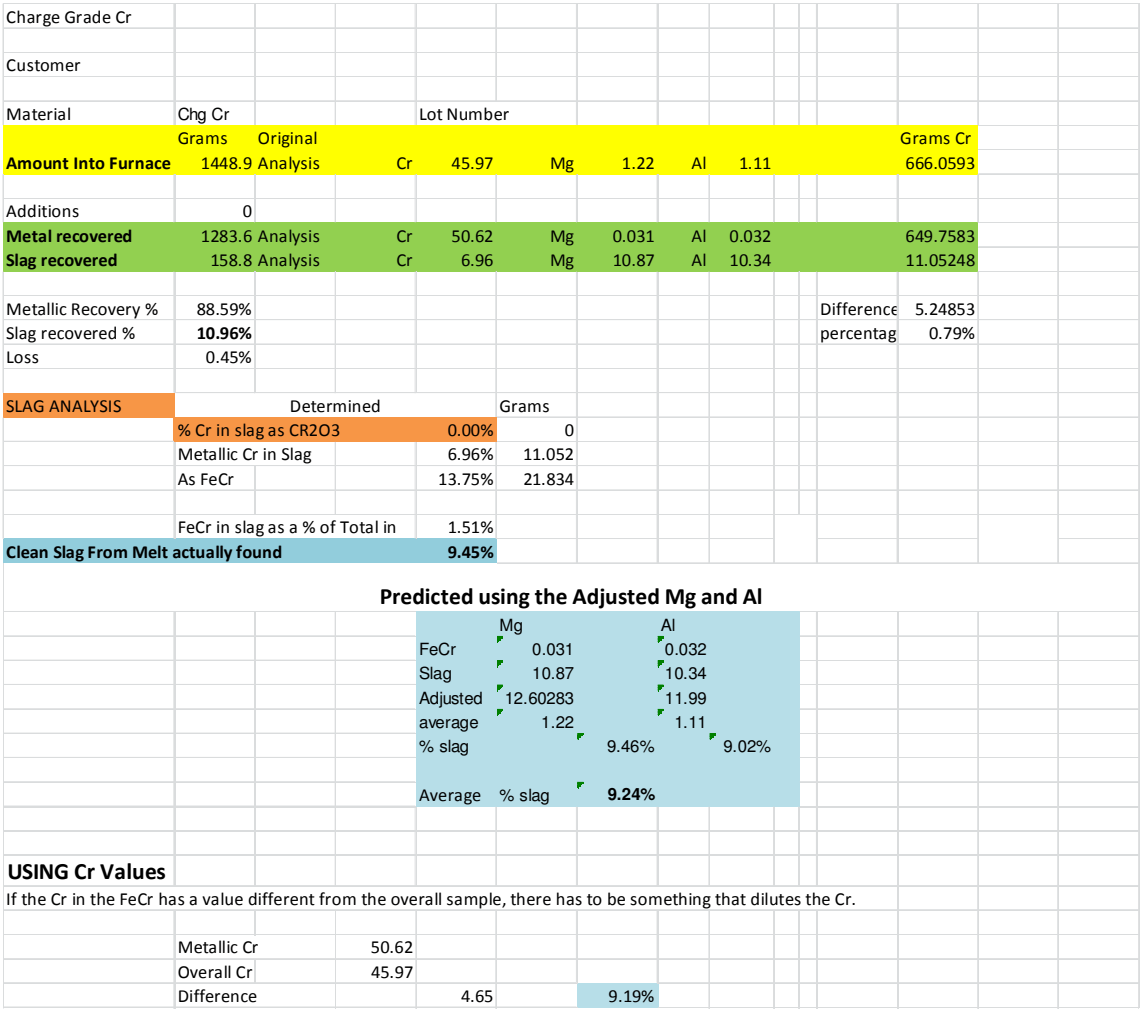
Example on Sample of Charge Chrome Fines

A barge load quantity of charge chrome fines was sampled at discharge for determination of elemental analysis and slag content. The methods described above were applied to the sample.

Table 1. Data Summary of Charge Chrome Fines Sample with High Slag Content

	Overall Sample	Metallic from Melt	Slag from Melt
Total Cr	45.97	50.62	6.96
C	5.70		
Si	5.49		
S	0.053		
P	0.014		
Al	1.11	0.032	10.34
Mg	1.22	0.031	10.87

Figure 1 - Calculations for High Slag Sample



Charge Grade Cr												
Customer												
Material	Chg Cr			Lot Number								
	Grams	Original										Grams Cr
Amount Into Furnace	1448.9	Analysis	Cr	45.97	Mg	1.22	Al	1.11				666.0593
Additions	0											
Metal recovered	1283.6	Analysis	Cr	50.62	Mg	0.031	Al	0.032				649.7583
Slag recovered	158.8	Analysis	Cr	6.96	Mg	10.87	Al	10.34				11.05248
Metallic Recovery %	88.59%									Difference		5.24853
Slag recovered %	**10.96%**									percentag		0.79%
Loss	0.45%											
SLAG ANALYSIS	Determined			Grams								
	% Cr in slag as CR2O3		0.00%	0								
	Metallic Cr in Slag		6.96%	11.052								
	As FeCr		13.75%	21.834								
	FeCr in slag as a % of Total in		1.51%									
Clean Slag From Melt actually found			**9.45%**									
Predicted using the Adjusted Mg and Al												
					Mg		Al					
				FeCr	0.031		0.032					
				Slag	10.87		10.34					
				Adjusted	12.60283		11.99					
				average	1.22		1.11					
				% slag		9.46%		9.02%				
				Average	% slag	**9.24%**						
USING Cr Values												
If the Cr in the FeCr has a value different from the overall sample, there has to be something that dilutes the Cr.												
	Metallic Cr	50.62										
	Overall Cr	45.97										
	Difference		4.65		9.19%							

Figure 1 - Calculations for High Slag Sample

Table 2. Data summary from Charge Chrome Fines sample with Low Slag Content

	Overall Sample	Metallic from Melt	Slag from Melt
Total Cr	48.06	50.54	11.58
C	7.15	7.85	1.57
Si	3.54		
S	0.049		
P	0.011		
Al	0.37	0.13	5.71
Mg	0.27	0.01	4.52

Charge Grade Cr														
Customer														
Material	Chg Cr			Lot Number										
	Grams	Original										Grams Cr		
Amount Into Furnace	1411.8	Analysis	Cr	48.06	Mg	0.27	Al	0.37	C	7.15		678.5111		
Additions	0													
Metal recovered	1314.7	Analysis	Cr	50.54	Mg	0.01	Al	0.13	C	7.85		664.4494		
Slag recovered	68.6	Analysis	Cr	11.58	Mg	4.52	Al	5.71	C	1.57		7.94388		
Metallic Recovery %	93.12%										Difference	6.11782		
Slag recovered %	**4.86%**										percentag	0.90%		
Loss	2.02%													
SLAG ANALYSIS	Determined				Grams									
	% Cr in slag as CR2O3			0.00%	0									
	Metallic Cr in Slag			11.58%	7.944									
	As FeCr			22.91%	15.718									
	FeCr in slag as a % of Total in			1.11%										
Clean Slag From Melt actually found				**3.75%**						**SLAG**	Approximately		**4%**	

Predicted using the Adjusted Mg and Al

	Mg	Al	
FeCr	0.01	0.13	
Slag	4.52	5.71	
Adjusted	5.86347	7.407171	
average	0.27	0.37	
% slag	4.44%	3.30%	
Average	% slag	**3.87%**	

USING Cr Values														
	If the Cr in the FeCr has a value different from the overall sample, there has to be something that dilutes the Cr.													
	Metallic Cr		50.54											
	Overall Cr		48.06											
	Difference			2.48		4.91%								

Figure 2 - Calculations for Low Slag Sample

Method Validation

Control Experiment

A sample of 2"x D Charge Chrome Lump was taken from stockpile for elemental and slag analysis. At this particle size, slag would be visually evident in the pile. Since little slag was observed by our sampler, other than the typical surface slag, the hypothesis is that little slag is present. A representative split of this sample was melted by induction furnace and the slag content determined by the previously described methods.

Table 3. Data summary for 2" x D Charge Chrome

	Overall Sample	Metallic from Melt	Slag from Melt
Total Cr	51.09	51.14	5.63
C	6.46		
Si	4.18		
S	0.045		
P	0.016		
Al	0.22	0.011	9.56
Ti	0.35		
V	0.30		
Mn	0.19		

Sn	<0.002		
Ni	0.16		
As	<0.002		
Fe	35.31		
O	0.68		
N	0.013		
Mg	0.20	0.006	9.32
Total	99.22		

Charge Grade Cr														
Customer			2" X down											
Material	Chg Cr			Lot Number										
	Grams	Original									Grams Cr			
Amount In	1418.2	Analysis	Cr	51.09	Mg	0.2	Al	0.22			724.5584			
Additions	0													
Metal recc	1407.7	Analysis	Cr	51.14	Mg	0.006	Al	0.011			719.8978			
Slag recov	13.7	Analysis	Cr	5.63	Mg	9.32	Al	9.56			0.77131			
Metallic Re	99.26%								Difference		3.88929	Grams		
Slag recov	**0.97%**								percentage		0.54%			
	-0.23%													
SLAG ANA		Determined			Grams									
	% Cr in slag as CR2O3			0.00%	0						**Slag From Melt**			
	Metallic Cr in Slag			5.63%	0.771						**Melt**		**0.86%**	
	As FeCr			11.01%	1.508						**Mg Al**		**1.90%**	
											Total Cr		**0.10%**	
	FeCr in slag as a % of Total in			0.11%										
Clean Slag From Melt actually found				**0.86%**							**Average Slag**		**1%**	
				Predicted using the Adjusted Mg and Al										
					Mg		Al							
				FeCr	0.006		0.011							
				Slag	9.32		9.56							
				Adjusted	10.47297		10.74265876							
				average	0.2		0.22							
				% slag		1.85%		1.95%						
				Average	% slag	**1.90%**								
USING Cr Values														
	If the Cr in the FeCr has a value different from the overall sample, there has to be something that dilutes the Cr.													
	Metallic Cr		51.14											
	Overall Cr		51.09											
	Difference			0.05		0.10%								

Figure 3 – Control Experiment Calculations

Alternate Technology

The theory was that none of the chrome found in the recovered slag was in oxide form. Traditional wet chemistry methods were unable to definitively say what state the chrome existed in the slag. The best technology to determine the chrome state is XRD. Samples of the recovered slag, recovered metal and original sample were sent to PANalytical for XRD analysis. PANalytical's evaluation of the material showed all chrome to be present in its metallic state.

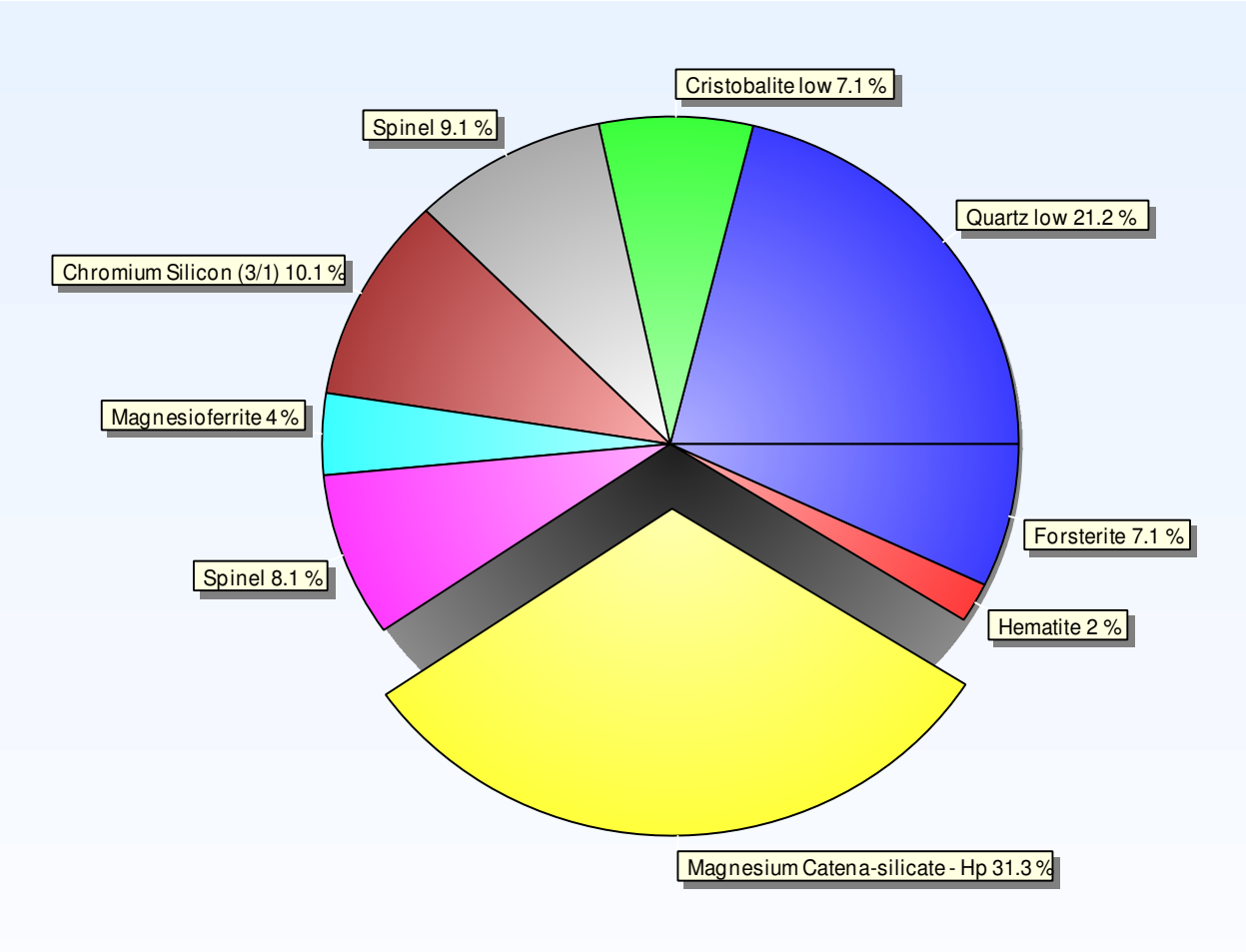


Figure 4 - XRD Summary of Slag Sample

Summary

Previous methodologies to estimate the amount of slag present in charge chrome relied on comparing of the concentrations of aluminum and magnesium in samples of the slag and pure material versus the concentration present in the overall sample. McCreath is of the opinion that the induction furnace method more closely reflects what the end user will experience with the charge chrome and is therefore the best way to separate the slag from the metal. It appears as though the estimation utilizing the concentration of aluminum and magnesium most likely overstates the amount of slag present. The chrome method is a good check method but likely grossly understates the slag content in the control experiment. It is best to take all three methods into account for the estimation of slag content so that no one method can impart any bias in the results.

Figure 5 - Charge Chrome Puck after melt

Figure 6 - View of puck after breaking to show the interior

References

Interview of personal communications

1. Andrews Bollenberg, private communication with George Wrightson, ELG Metals, July 2011.
2. ASTM E363, Vol 03.05
3. ASTM E32, Vol 03.05
4. Thermo ICAP 6300 Operators Manual

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