Hygroscopic Moisture Determination of Groote Eylandt Manganese Ores

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Abstract

Hygroscopic moisture is not widely understood and accounted for in the analysis of manganese content in manganese ores. Some manganese ore types are very hygroscopic in nature and this characteristic must be taken into account for correctly determining the contained manganese content of the traded commodity. Some of the international standards governing the analysis of manganese ores are not necessarily applicable to ores with significant hygroscopic moisture content. Groote Eylandt Mining Company (BHP-GEMCO) has worked with several of its customers on this issue and has improved understanding of hygroscopic moisture and its impact on analytical agreement.

Introduction

A material is considered to have a hygroscopic nature where it has the ability to adsorb water from the atmosphere while still maintaining its apparent dry appearance.

The adsorption of moisture by bulk manganese products is negligible. However when the surface area of a material is increased through the reduction of particle size, the effects of adsorption of moisture can become significant for some manganese ores. This is of particular relevance when ores have been finely pulverised in preparation for analysis. The pulverising action greatly increases the surface area of the sample thus increasing exposure to moisture from the atmosphere.

Where a material mass is small, as is typical for analytical test portions, changes in weight due to the adsorption of moisture may impact on analytical results. In the case of hygroscopic ores, the weight of an analytical test portion will increase over time as moisture is adsorbed from the atmosphere until the ore equilibrates with the atmosphere.

Commercial agreements for the trading of manganese ores are based on payment being made on a "dry mass basis." This understanding needs to be correctly reflected in the treatment of a test portion used in the analytical determination for ascertaining the contained metal content of the traded commodity.

If not correctly considered, an analytical test portion which is assumed as being one hundred percent dry, may in fact contain a significant quantity of water. The analytical test portion instead of being pure ore may be a mixture of ore and water, with the net effect being the understating of the contained elemental concentration.

As there is no visual indication that a material has or has not adsorbed moisture, unless correctly understood the effects of hygroscopic moisture are not often considered.

Hygroscopic Nature Of Groote Eylandt Ores

When compared with other major sources of manganese ores, when dried and then reduced to a pulverised form, Groote Eylandt ores will rapidly adsorb water from the atmosphere. Some Groote Eylandt ore types will adsorb over 1% of moisture where as South African manganese ores will typically adsorb between 0.1 to 0.2% moisture (Fig.1.).

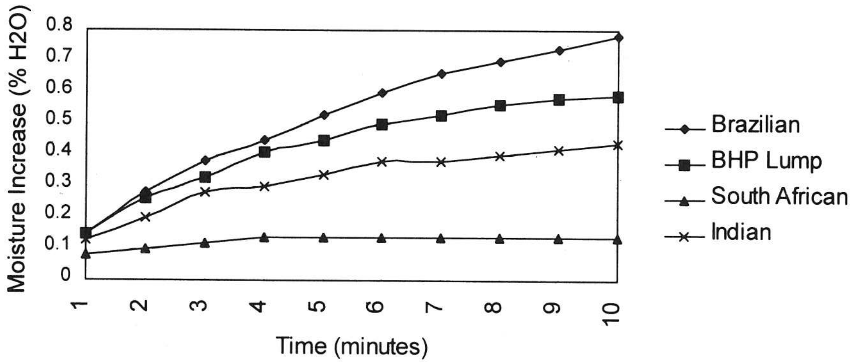
BHP-GEMCO studies have demonstrated that the final hygroscopic moisture uptake is independent of the atmosphere. What is determined by the atmospheric influence is the rate of re-hydration of the dried material.

When related to a 50% Mn product, a 1% uncorrected hygroscopic moisture content would equate to a 0.5% manganese difference between the reported manganese content of a test portion and the true manganese content of a test portion.

Assumed Dry Mass vs Hygroscopic Moisture Measurement

Although there are a number of methods for the pre treatment of a sample for analysis, there are fundamentally two approaches to the reporting of analysis of a commodity on a dry mass, namely pre drying and mathematical correction.

Figure 1. Hygroscopic moisture uptake for various manganese ores on exposure to the atmosphere after drying



Pre Drying

Typical free moisture is removed from samples as part of the process to facilitate effective preparation of a representative sample. At the completion of removing free moisture the material is one hundred percent dry. However on pulverising, hygroscopic ores will rapidly adsorb moisture from the air.

In some cases the analysis is conducted on samples at this stage of preparation. The results of such analysis would certainly be understating the true result due to moisture being weighed as part of the mass of the test portion.

Another variation of this same approach is for a portion of the sample to be redried when the sample is received in the laboratory for analysis. When dried, the material is allowed to cool to room temperature in a desiccator prior to weighing for analysis. This approach would be applicable to non hygroscopic ores but there are associated risks with this approach for hygroscopic ores.

In the case of Groote Eylandt ores, the potential for hygroscopic moisture uptake is high and moisture is adsorbed even within a strong desiccating environment such as when using silica gel and magnesium perchlorate. Moisture is adsorbed by the ore from the desiccants. A further risk is the weight change of test portions during weighing for analysis. As the material is not in a steady state equilibrium, the mass of a test portion will increase over time.

Mathematical Correction

The second approach to reporting analysis on a dry mass basis is to measure the hygroscopic moisture content of the test material simultaneously with the analysis. A mathematical correction is then applied to report the final result to a dry mass basis.

The standard which governs the determination of hygroscopic moisture for manganese ores is ISO 310, "Manganese Ores And Concentrates - Determination Of Hygroscopic Moisture Content In Analytical Samples - Gravimetric Methods."
The basis for ISO 310 is that a hygroscopic moisture determination is performed in parallel with the analysis of the manganese ore. Test portions for the hygroscopic moisture content are weighed at the same time as those for the analytical determination. The result of the hygroscopic moisture determination accurately accounts for the hygroscopic moisture content of the analytical test portion at the time of analysis. The result of the hygroscopic moisture determination is used to correct the results of the analytical determination to a "dry mass basis."

What is not clearly defined in ISO 310 is the equilibration of the sample material in the testing environment. It is a fundamental principle that analytical test portions are in a steady state of equilibrium when weighing.

In summary, the approach of minimising the effects of moisture by pre drying test material is applicable only to ores with a low hygroscopic content, where any uptake of hygroscopic moisture will not have a measurable affect on analytical results.

The approach of pre drying test material is not applicable for manganese ores with a high hygroscopic moisture potential. Although pre drying may minimise the impact of hygroscopic moisture, the effectiveness of pre drying for each determination is unquantifiable.

For hygroscopic ores, the only true way of expressing a result as a "dry mass basis," is the accurate measurement and correction of the hygroscopic moisture content of the test portion at the time of analysis, as per ISO 310.

Gemco Analysis Study

In 1994/95 Gemco undertook the organisation of an interlaboratory test program to examine the analysis of manganese ores. The aim of the program was primarily to provide the opportunity for individual laboratories to rank the accuracy and precision of their analysis against that of other participants.
A set of five samples of various Groote Eylandt manganese ores was sent to each of the participants for the determination of manganese, iron, silica alumina, phosphorus and hygroscopic moisture. The analysis of each sample was requested to be conducted in quadruplicate with the results being expressed as corrected and uncorrected for hygroscopic moisture.

Invitations to participate were extended to organisations who were end users of manganese ores or had an active interest in the analysis of manganese ores. The participants included alloy producers, superintendent companies and laboratories from Australia, Japan, Korea, North America, Norway and the United Kingdom.

The program developed into a significant study of manganese analysis with a total of twenty four organisations participating in the test program incorporating a wide range of analytical methodologies and standards. The large number of participants allowed for a meaningful statistical evaluation to be conducted on the results. The results of the program provided an invaluable platform for further examination of differences in analytical methodology.

One of the predominate observations from the interlaboratory program was the impact of the hygroscopic moisture correction on the reported result for the elements of consideration. It was observed that in some of the results which were returned, poor accuracy in the manganese result was not necessarily because of the manganese determination. In some instances the manganese accuracy had been impacted by the incorrect consideration of the hygroscopic moisture correction.

Case Study Of Hygroscopic Moisture Determination

BHP-GEMCO embarked on a program to further investigate some of the findings and observations from the interlaboratory program with its customers. The following is a case study of such an investigation which GEMCO undertook with two ferro alloy plants.

A review of results from the interlaboratory program showed a strong systematic difference in the reported manganese result between Gemco and the two ferro alloy plants (Table 1). A review of shipping results also demonstrated the same strong systematic difference (Table 1).

The laboratories of all three operations determined manganese content by potentiometric titration using similar instrumentation and methodologies. All three laboratories were also accounting for hygroscopic moisture content of the test portion for analysis.

A representative from each operation was nominated and a project team was formed to investigate the ongoing difference in manganese results for shipments.

Based on the observations from the interlaboratory test program, the project team considered that there was strong evidence that there were anomalies within the hygroscopic moisture determination.

It was evident that all three laboratories were achieving similar levels of precision for the manganese determination but Gemco was achieving significantly better precision in the hygroscopic moisture determination compared with the two ferro alloy plants.

All three laboratories were determining hygroscopic moisture using ISO 310. However there were a number of "in house" adaptations of the method which provided the opportunity for some subtle differences in techniques.

The hygroscopic moisture absorption rate of a sample is dependent on the treatment of the sample at the time of analysis. The equilibrating process allows the hygroscopic moisture content of a

Table 1. Manganese analyses differences (% Mn) between GEMCO and Alloy Plants

Interlaboratory Test Programme Summary					
Test Sample	GEMCO	Plant A	Plant B	Difference GEMCO/ Plant A	Difference GEMCO/ Plant B
Sample A	51.698	51.670	51.503	0.028	0.195
Sample B	45.768	45.645	45.583	0.123	0.185
Sample C	49.843	49.723	49.580	0.120	0.263
Sample D	44.710	44.610	44.440	0.100	0.270
Sample E	43.295	43.105	43.060	0.190	0.235

Average difference GEMCO/Plant A -	0.112	
Average difference GEMCO/Plant B -		0.230
Average Manganese Difference for Shipments Prior to Study		
Average difference GEMCO/Plant A -	0.115	
Average difference GEMCO/Plant B -		0.221
Average Manganese Difference for Shipments After Study		
Average difference GEMCO/Plant A -	0.063	
Average difference GEMCO/Plant B -		0.021

sample to reach a steady state prior to analysis.

Once a steady state equilibrium has been reached, the analytical test portions for the hygroscopic moisture and manganese determinations need to be weighed together to minimise any further change in the equilibrium state of the samples. The result of the hygroscopic moisture determination reflects the hygroscopic moisture content of the test portion at the time of analysis.

There was an inconsistent approach to the equilibrating process by the three laboratories. One approach being that samples were analysed on an "as received basis" where analytical test portions were weighed without the sample material reaching a steady state equilibrium. In this case there is a risk of the samples undergoing change between weighing and the separate hygroscopic moisture and manganese determinations.

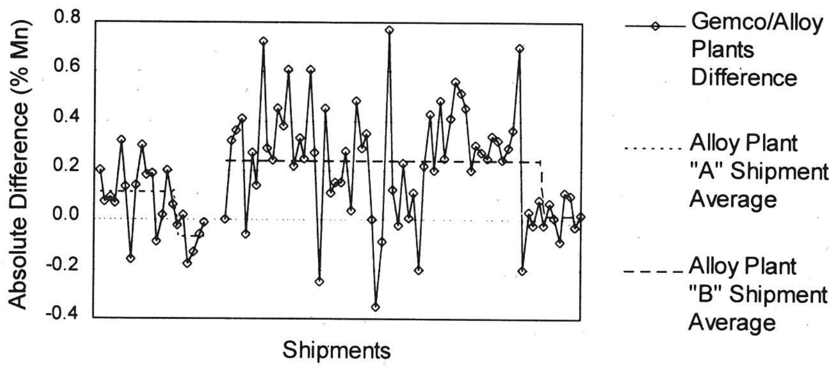
There were also technique differences between the three laboratories in the weighing back of the sample after drying. After the sample for hygroscopic determination has been dried and allowed to cool in a desiccator, the weighing vessel containing the sample is then weighed. Just prior to weighing, the lid of the weighing vessel is momentarily loosened to release any internal pressure which may have accumulated during the drying and cooling process. Once the pressure has been released it is important that the lid is returned to the vessel to prevent any further adsorption of moisture.

The study group undertook the standardisation of techniques used in the hygroscopic moisture determination.

Standardisation of techniques included:-

- Allowing the test portion to equilibrate in the laboratory atmosphere prior to weighing and drying.
- Consistent drying and cooling times.

Figure 2. Manganese difference for shipments samples between GEMCO and alloy plants



- Equalisation of air pressure in weighing vessels post drying and prior to final weighing.
- Minimisation of readsorption of hygroscopic moisture post drying and prior to final weighing.
- Uniformity in glass weighing vessels used in the determination.

The standardisation of techniques were implemented for shipment samples. The average manganese shipment analysis difference between BHP-GEMCO and alloy plant "A" has been reduced from 0.12% Mn to 0.06% Mn and for alloy plant "B" the average difference has been reduced from 0.24% Mn to 0.02% Mn (Table 1. and Figure 2.).

As a result of mutual effort, analytical confidence has been improved between the three operations and is demonstrated by the close agreement in shipments results.

This case study highlights a number of important issues. These issues being:-

- The impact of the hygroscopic moisture correction on the reported manganese when analysing Groote Eylandt ores.
- Although all three laboratories were conducting hygroscopic moisture determination the method was found to be sensitive to subtle technique differences.
- The usefulness of benchmark data gathered from the interlaboratory program in identifying differences and analysing variation in analysis techniques.
- The opportunity to improve the quality of analytical results and achieve a higher level of confidence through co-operative investigations of analysis methods.
- The forum for discussing hygroscopic moisture provided the opportunity for discussion on other areas of analytical difference and experience sharing.

Conclusion

The hygroscopic moisture content of analytical test portions needs to be correctly considered when analysing Groote Eylandt manganese products. A valid analysis can only be performed by the accurate determination of the hygroscopic moisture content of test portions at the time of analysis as prescribed by ISO 310. Correct determination of hygroscopic moisture content by ISO 310 is technique sensitive and close attention to techniques is require when performing the analysis.

If hygroscopic moisture is not accurately accounted for during analysis, the true value of the contained manganese content of a product will not be correctly stated.

References

Standards

ISO 310 Third Edition 1992-11-01, "Manganese Ores And Concentrates - Determination Of Hygroscopic Moisture Content In Analytical Samples - Gravimetric Methods."

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JIS M 8203 - 1982, "General Rules For Chemical Analysis For Manganese Ores."

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