

IMPLICATIONS OF CURRENT REACH AUTHORIZATION REQUIREMENTS FOR ORES, CONCENTRATES AND MINERALS

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SUMMARY

To provide a perspective on the difficulties of authorizing ores, concentrates and minerals under REACH as it is currently envisaged, Mintek with the support of several industry representatives conducted a survey of the chemical and mineralogical properties of a number of ores, concentrates and minerals that are currently exported to the EU or that may potentially be exported to the EU. Mineralogical- and compositional-data were obtained for several commodities (iron ore, manganese ore, coal, lead concentrate, antimony concentrate, PGM concentrate, chromite, zircon and rutile). For all the commodities that were studied the intrinsic mineralogical complexities lead to unanticipated variations in chemical composition. For the interested reader details of these complexities are given in the body of the report. In this summary section examples are given of the mineralogical and chemical complexity in the context of REACH as it is currently envisaged.

Installations that use ores, concentrates and minerals

The industrial activities in terms of EU directive 96/61/EC-IPPC (Annex 1) that would use the ores, concentrates and minerals evaluated in this study are given in Table 1.

Table 1. Industrial activities in the EU that use ores, concentrates and minerals.

Commodity	Industrial activity
Manganese ore	Production and processing of metals 2.3 Installations for the processing of ferrous metals 2.4 Ferrous metal foundries with a capacity exceeding 20 tonnes per day 2.5 Installations (a) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes. (b) For the smelting, including the alloyage, of non-ferrous metals Chemical industry 4.2 Chemical installations for the production of basic inorganic chemicals such as: Salts (d)
Iron ore	Production and processing of metals 2.3 Installations for the processing of ferrous metals 2.4 Ferrous metal foundries with a capacity exceeding 20 tonnes per day
Coal	Energy industries 1.1 Combustion installations with a rated thermal input exceeding 50 MW Mineral industry 3.1. Installations for the production of cement clinker in rotary kilns

Table 1, continued

<p>PGM concentrates</p>	<p>Production and processing of metals 2.1 Metal ore roasting or sintering installations 2.5 Installations (a) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes. Chemical industry 4.2 Chemical installations for the production of basic inorganic chemicals such as: Salts (d)</p>
<p>Chrome</p>	<p>Production and processing of metals 2.3 Installations for the processing of ferrous metals 2.4 Ferrous metal foundries with a capacity exceeding 20 tonnes per day 2.5 Installations (c) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes. For the smelting, including the alloyage, of non-ferrous metals Mineral industry 3.3 Installations for the manufacturing of ceramic products by firing, in particular roofing tiles, bricks, refractory bricks, tiles, stoneware or porcelain Chemical industry 4.2 Chemical installations for the production of basic inorganic chemicals such as: Salts (d)</p>
<p>Antimony oxide</p>	<p>Production and processing of metals 2.2 Metal ore roasting or sintering installations 2.5 Installations b) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes. Chemical industry 4.2 Chemical installations for the production of basic inorganic chemicals such as: Salts (d)</p>
<p>Zircon</p>	<p>Production and processing of metals 2.5 Installations (b) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes. Mineral industry 3.4 Installations for the manufacture of glass including glass fibre 3.5 Installations for melting mineral substances including the production of mineral fibre 3.6 Installations for the manufacturing of ceramic products by firing, in particular roofing tiles, bricks, refractory bricks, tiles, stoneware or porcelain Chemical industry 4.3 Chemical installations for the production of basic inorganic chemicals such as: Salts (d)</p>

Table 1, continued

Lead concentrate	Production and processing of metals 2.3 Metal ore roasting or sintering installations 2.5 Installations (b) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes. Chemical industry 4.2 Chemical installations for the production of basic inorganic chemicals such as: Salts (d)
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Variability

Variability between deposits

Unlike chemicals which are inherently homogeneous in composition and are the products of well-controlled production plants, ores and concentrates are inherently heterogeneous in composition owing to the fact that they comprise suites of minerals, each mineral with a unique composition. As a result of geological differences between ore bodies the types and relative amounts of ore- and gangue-minerals will be different for different deposits of the same commodity. This principle is well illustrated by the manganese deposits that are currently mined in South Africa. In the so-called 'Mamatwan' type the major ore minerals are braunite (Mn_7SiO_{12}), kutnahorite ($Ca(Mn,Fe,Mg)(CO_3)_2$) and hausmannite (Mn_3O_4) and in the so-called Wessels type the major ore minerals are braunite II ($Ca(Mn,Fe)_{14}SiO_{24}$), bixbyite ($(Mn,Fe)_2O_3$) and hausmannite (Mn_3O_4). It stands to reason that the amounts and types of gangue minerals will also be different in the two ore types. As a result of the differences in the mineralogical make-up of the two ore types they have different compositions (Mamatwan ore typically contains about 39% Mn and Wessels ore contains about 48% Mn).

However, it is not just the concentrations of the valuable elements that are different between the ore types, the levels of carcinogenic, mutagenic and reprotoxic (CMR) substances. This is clearly illustrated by data for platinum group metal concentrates (Table 2), which show that there are order-of-magnitude differences in the concentrations of CMR substances between the deposits.

Table 2. Concentrations of Ni, As, Co and Pb in platinum group metal (PGM) concentrates from different deposits.

Element	Deposit I	Deposit II	Deposit III	Deposit IV
Ni (%)	2.3	11.7	4.5	0.4
Cr (%)	1.3	0.3	0.25	2.53
As (ppm)	312	12	36	30
Co (ppm)	495	240	1300	not available
Pb (ppm)	527	148	1600	182
Mn (ppm)	500	400	900	not available

Variability within a deposit

Mineralogically-driven differences and complexities are unfortunately not limited to different ore bodies and ore types; there are also significant variations in the amounts and proportions of minerals within a particular ore type. These ‘local’ differences are caused by localized geological features such as faults with their associated alteration zones, near-surface oxidation, the intrusion of dykes, etc. Detailed data for different types of Wessels ore offer a good example of ‘localized’ compositions differences (Table 3). The data show that within a deposit the concentrations of CMR substances in different ore types can vary over an order-of-magnitude, i.e., the variability within an ore-type can be as severe as the variability between ore types. Furthermore, in most instances the variability for a specific ore type exceeds the permitted variability (PV).

With regard to the data in Table 3 the variation in the concentration of boron it is of particular significance. In some ore types the concentration is almost an order-of-magnitude below the authorization threshold (0.1%) but in the ‘braunite’ ore type it is well above the threshold. To further complicate the matter the variance in the concentration of boron exceeds the permitted variability for most ore types.

In summary, there is overwhelming evidence that the variability between ore bodies and within a particular ore type can be much bigger than the permitted variability.

Table 3. Concentrations of SiO₂, TiO₂ and B in different types of ‘Wessels’ manganese ore.

	Mean value	Variance (%)	Permitted variability (%)	PV
<i>Ore type:</i>	Braunite-calcite-hausmannite			
SiO ₂ (%)	6.91	17	20	< PV
TiO ₂ (%)	0.03	33	30	> PV
B (ppm)	421	12	30	< PV
<i>Ore type</i>	Braunite II-Hausmannite			
SiO ₂	2.71	74	20	> PV
TiO ₂	0.04	50	30	> PV
B (ppm)	238	32	30	> PV
<i>Ore type</i>	Hausmannite-Bixbyite			
SiO ₂	1.03	68	30	> PV
TiO ₂	0.06	50	30	> PV
B (ppm)	330	45	30	> PV
<i>Ore type</i>	Hausmannite			
SiO ₂	0.2	50	30	> PV
TiO ₂	0.02	250	30	> PV
B (ppm)	155	77	30	> PV
<i>Ore type</i>	Braunite			
SiO ₂	9.32	32	20	> PV
TiO ₂	0.04	125	30	> PV
B (ppm)	1528	39	30	> PV

Mineralogical complexity of ores and concentrates

With regard to the complexity of ores, concentrates and minerals one of the aspects that must be clarified is the interpretation of the 0.1% threshold for the concentration of CMR compounds that will trigger authorization. In many cases the concentration of one of the CMR compounds consistently exceeds the 0.1% threshold and the status of such materials is clear. However, there are many other cases where the sum of the concentrations of different compounds may exceed the authorization threshold or, with respect to permitted variability, elevate the total concentration of CMR compounds to levels where a lower variability is permitted. Examples where the sum of CMR compounds may trigger authorization or lead to a lower permitted variability are given in Table 4.

For the PGM concentrate the sum of the CMR compounds is greater than 2.5%, which means that the permitted variability is 20%, rather than 30% as it would have been if the individual CMR compounds above 0.1% were considered. For the manganese ore none of the CMR compounds are above 0.1% but the sum is above 0.1%.

Table 4. Examples of commodities where the sum of the concentrations of CMR compounds will have an impact on how the materials are dealt with under REACH.

Commodity	Ni (%)	Co (%)	Mn (%)	As (%)	Pb (%)	B (%)	Cr (%)	Σ CMR
PGM conc.	2.3	0.054	0.05	0.031	0.053	-	1.3	3.789
Mn ore	0.003	0.007	-	-	0.002	0.093	0.001	0.106

PGM conc. is a platinum group metals concentrate

Mn ore is a manganese ore of the Mamatwan type

Σ CMR is the sum of the concentrations of CMR compounds (%)

The complex mineralogical nature of ores and concentrates means that the information in a bulk chemical analysis often does not describe the way in which the elements occur in the material. Conventionally, chemical compositions of ores, minerals and concentrates are expressed as oxides, even if the material does not contain those oxides is distinct species. For example, the concentration of the element silicon (Si) in an ore, mineral or concentrate would be expressed as 'SiO₂' even though the materials may not actually contain crystalline silica (alpha-quartz) as a discrete mineral type. The way the bulk chemical data is presented is simply a convenient nomenclature that has been universally adopted and it has no bearing on the mineral phases that are present in the material. Therefore, in many cases the CMR or PBT toxicity can not be judged from the concentrations of chemical elements present since it does not provide information on the form in which the elements are contained in the material.

Examples where the chemical composition does not accurately reflect the mineral form are found in all the commodities that were examined in this report. Manganese ores contain silica-bearing manganese-oxide minerals; braunite (Mn²⁺Mn₆³⁺SiO₁₂) and braunite II (Ca_{0.5}Mn₇³⁺Si_{0.5}O₁₂). In iron ores at least a portion of the silica is present in micas, which are silicate minerals with complex compositions. That some or all of the SiO₂ may be contained in micas rather than perhaps quartz can not be deduced from the bulk composition. In zircon (ZrSiO₄) the deportment of SiO₂ is even more complex since most of the 'SiO₂' reported in a chemical analysis of a zircon concentrate sits in the crystal lattice of the mineral zircon. This is analogous to the SiO₂ in glass, it is not present as a pure oxide but in a complex chemical 'mixture'. However, in a zircon concentrate not all the silica occurs in the mineral zircon and some of the SiO₂ reported in a chemical analysis might actually be present in quartz or other silicate minerals that are intergrown

with zircon grains and the measurement of 'non-zircon silica' is subject to considerable uncertainty.

Another instance where the CMR element lists cannot be directly applied to ores and concentrates is presented by 'TiO₂'. TiO₂ pigment, which is ultra-fine and ultra-pure has been identified as a possible carcinogenic substance but ores and concentrates never contain ultra-fine and ultra-pure TiO₂. As with alpha-quartz, the properties of TiO₂ as a nano size chemical are not the same as those of naturally occurring minerals such as rutile and the properties of the chemical cannot be applied to natural minerals.