CANADIAN CERTIFIED REFERENCE MATERIALS

Certificate of Analysis

FOUR NORTH-AMERICAN BY-PRODUCT REFERENCE GYPSUM SAMPLES TYPE : CALCIUM SULFATE DIHYDRATE, $CaSO_4 . 2H_2O$ FGD-1, FGD-2, TIG-1 and GYP-4

These Certified Reference Materials (Standards) were prepared and issued by the Analytical Group of Domtar Inc. Research Center in Senneville, (Montreal), Quebec, Canada in cooperation with the Domtar Gypsum Products Division in Ann Arbor, Michigan, U.S.A. The 'round-robin' analyses of the bulk sample were kindly carried out by eighteen participating laboratories. The results received from the 'round-robin' were statistically evaluated and are presented in this document.

The Certified Reference Materials are intended for the determination of major, minor and trace elements in by-product gypsum by various analytical methods. Another application is in environmental and quality control analysis of flue-gas by-product gypsum or from titanium dioxide production plants. Combined together with the already existing Certified natural gypsum standards (3), these can be used for the calibration of process equipment and analytical methods in industry and research.

THE ORIGIN OF THE SAMPLES

Three samples originate from plants located in the U.S.A. and one from a plant in Canada. Two of the samples are of the FGD (flue gas desulfurization) type and the other two, TIG-1 and GYP-4 are titano-gypsum (by-product gypsum from titanium dioxide,TiO2 production). The FGD-1 bulk sample originated from a double-alkali process for SO2 absorption at a large electric power station in Indiana. Sample FGD-2 was obtained from a power station in Florida, where the desulfurization system was of double-loop design. Ground limestone slurry made from treated wastewater effluent was used for scrubbing. Gypsum TIG-1 originated as a by-product from a titanium dioxide (anatase) production plant in Georgia, U.S.A. GYP-4 is a by-product gypsum from TiO2 (rutile) production in Quebec. The last two samples were result of neutralization of spent sulfuric acid by limestone, CaCO3. Sample TIG-1 is particularly interesting, because it contains high levels of trace elements not observed in natural gypsum. On the other hand, sample GYP-4 is almost 100% pure gypsum.

PREPARATION OF THE SAMPLES

Each of the three (60kg) samples were chosen from bulk production material weighing several tons.. The samples were dried at 40°C for 48 hrs, thoroughly mixed and homogenized in a stainless steel blender, then tested for homogeneity by X-ray Fluorescence Spectrometry. The homogeneity of the two samples FGD-1 and TIG-1 was not satisfactory after the initial quartering and mixing, therefore the samples were carefully ground (without overheating) in a large ALPINE pulverizer to –200 mesh (74 microns). Because of their high homogeneity samples FGD-2 and GYP-4 were not ground. Their particle size distribution corresponds to the original production sample.

STABILITY AND INSTRUCTIONS FOR STORAGE AND DRYING

The long term stability of the samples was not rigorously tested, but it is known from experience that these should last for a long period of time (many years), provided that the storage temperature is kept around 20 – 25°C and the samples are not exposed to direct sunlight, or sources of heat.

ATTENTION – VERY IMPORTANT: The bottled samples are supplied already dried for you at 40°C. If necessary, samples can be dried for a minimum of 1 hour at 40°C ± 3°C. Sufficient drying is completed in 2 to 6 hours depending on the amount of sample and moisture absorbed. In no circumstances should the temperature of drying exceed 50°C. Overdrying of the samples or the use of excessive temperatures will cause decomposition of gypsum, CaSO4.2 H2O into hemi-hydrate CaSO4.½ H2O and into anhydrite CaSO4. The samples should be therefore stored away from direct sunlight and sources of heat. It is recommended that the bottle is tightly closed after each use.

QUANTITY AND PACKAGING

The samples are packaged for laboratory use in 100g ± 0.5g quantities. Polyethylene bottles were chosen for easy transportation.

LOSS ON IGNITION AND RESIDUAL CALCIUM SULFITE, CaSO3 ½ H2O

Loss on ignition was determined by several laboratories on the dried sample heated for one hour at 1000°C. The 'loss on ignition' (L.O.I.) values may be important for laboratories using borate fusion as a sample preparation method (1) for multielement X-ray fluorescence analysis of gypsum (2, 3). Tests carried out on gypsum by thermal analysis (DTA-TGA) confirmed that the final product of gypsum dehydration and ashing i.e. anhydrite, CaSO4 is stable up to 1200°C. Dissociation into CaO and SO3 begins only above this temperature. Tests for residual calcium sulfite, CaSO3.1/2 H2O showed levels less than 0.05% present in samples FGD-1 and FGD-2.

ANALYTICAL METHODS

The analytical methods used by the participating laboratories varied from the classical 'wet chemical' methods to the most modern instrumental methods known today. The variety of methods included gravimetry, atomic absorption spectrophotometry (AA), X-ray fluorescence spectrometry (XRF), inductively coupled plasma emission (ICP), thermal analysis (DTA-TGA), coulometry, selective ion electrode methods and gas evolution techniques. Several laboratories determined the trace element concentrations by neutron activation analysis (INAA), other participants used spectroscopic methods.

STATISTICAL EVALUATION OF THE ROUND-ROBIN RESULTS

The individual results received from the participating laboratories were processed by the computer program CERTIFIC, written for the IBM/PC compatible systems by Rousseau (4). The basic ideas and the statistical functions of the program were based on work published by Dybczynski (5). The Dybczynski-Rousseau computer program uses different statistical criteria for the rejection of 'outliers'. These are Dixon's and Grubb's criteria, followed by tests for 'normal distribution', 'skewness' and 'kurtosis' of the data.

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ISSUE DATES OF CERTIFICATES

Senneville, Quebec, Nov. 1991 (original issue date)
Montreal, Oct. 2004 (verified and one trace element value deleted, other values remain unchanged)

REFERENCES

(1) Claisse Fluxer-Bis, Corporation Scientifique Claisse, Ste-Foy, Quebec, Canada

(2) Kocman V., "Rapid Multielement Analysis of Gypsum and Gypsum Products by X-ray Fluorescence Spectrometry" : A.S.T.M. STP-861, pp. 72-83, 1961 Race St. Philadelphia, PA, 19103 U.S.A. (1984)

(3) Kocman, V. and Foley, L.M., Geostandards Newsletter, Vol. 11, No. 1, 87-102 (1987)

(4) IBM/PC software from Les Logiciels R. Rousseau Inc., 28 Montmagny, P.O. Box 394, Cantley, Quebec, Canada J0X 1L0

(5) Dybczynski R., Analytica Chimica Acta, 117, 53-117 (1980)

CERTIFIED VALUES

(all values are based on a sample dried at 40°C)

MAJOR ELEMENTS IN WEIGHT PERCENT

(Std. deviations in parentheses refer to the last decimal place)

	FGD-1		FGD-2		TIG-1		GYP-4	
CaO	32.7	(1)	32.8	(0.1)	32.3	(1)	32.2	(2)
SO_3	46.4	(2)	45.6	(2)	43.4	(3)	46.3	(2)
MgO	0.007	(1)	0.019	(2)	0.12	(2)	trace	
Al_2O_3	0.023	(4)	0.033	(3)	0.57	(2)	trace	
Fe_2O_3 T *	0.014	(1)	0.043	(3)	0.26	(1)	trace	
P_2O_5	0.03	(1)	0.05	(1)	0.04	(1)	<0.01	
SiO_2	0.13	(1)	0.21	(2)	0.11	(3)	0.02	(1)
K_2O	0.007	(2)	0.01	(05)	0.008	(3)	trace	
Na_2O	0.005	(1)	0.02	(1)	0.036	(2)	trace	
SrO	0.012	(1)	0.024	(1)	0.42	(2)	0.42	(1)
V_2O_5	0.0003	(07)	0.0009	(2)	0.10	(1)	trace	
Cr_2O_3	0.0002	(01)	0.0015	(2)	0.036	(3)	trace	
TiO_2	trace		trace		0.82	(4)	trace	
H_2O +	20.70	(7)	20.38	(5)	20.3	(1)	20.85	(1)
CO_2	0.02	(04)	0.62	(3)	1.41	(7)	0.02	(1)
% Total:	**100.05**		**99.81**		**99.93**		**99.81**	
% L.O.I. **	21.04	(5)	21.33	(5)	22.03	(03)	20.91	(2)

* Total iron calculated as Fe_2O_3
** Loss on ignition at 1000°C (1hr)
H_2O+ Combined water determined at 250°C

TRACE ELEMENTS IN ALPHABETICAL ORDER

Mean concentrations in micrograms/gram (µg/g)

Element	FGD-1	FGD-2	TIG-1	GYP-4
As	0.10	0.48	0.22	<0.01
Ba	-	-	-	23
Cd	-	-	-	<0.2
Ce	0.7 (0.2)	1.18 (0.22)	6 (0.8)	-
Cl	100?	115?	400	<5
Co	0.02	0.07	0.26	<0.1
Cr	1.2	10.2	246	2.4
Cu	-	-	-	<10
Dy	-	0.48	0.42	0.14
Eu	0.02	0.09	0.08	-
F	95	320	230	<25
Fe	-	-	-	38
Hg	-	-	-	<0.1
K	-	-	-	10
La	0.35	2.18	2.7	0.6
Lu	0.006 ?	0.007 ?	0.03 (0.01)	0.06 (0.01)
Mg	-	-	-	<60
Mn	2.0	2.5	35	0.81
Na	-	-	-	10
Sb	0.03	0.024	0.05	0.009
Sc	0.023	0.166	17	0.24
Se	0.8	3.0	-	<0.3
Sm	0.07	0.52	0.65	-
Ta	-	-	3.1	-
Th	0.03	0.38	2.14	<0.02
Ti	75	75	TiO2 above	21
U	-	1.10	2.5	<0.2
V	15	5.1	560	3.1
Yb	-	0.27	0.31	-
Zn	1.7	2.3	32?	0.5
Zr	-	10?	80?	<5

? Provisional value only, less than 5 results available, or std. deviation too high
\- Value not available

PARTICIPATING LABORATORIES

The round robin analyses were performed by the following laboratories, whose help with the project is greatly appreciated. Their list is provided in alphabetical order.

BRITISH GYPSUM LTD. Research and Development, East Lake, United Kingdom (Mr. A Conway)

BRITISH GEOLOGICAL SURVEY Keyworth, Nottingham, United Kingdom (Mr. M.N.Ingham)

CANMET Energy Mines and Resources, Minerals Laboratory, Ottawa, Ontario, Canada (Mr. J.C. Hole)

DOMTAR INC. Gypsum Products Laboratory, Caledonia, Ontario, Canada (Mr. Francis Vrillaud)

DOMTAR INC. Research Center, Analytical Laboratory (Dr. V. Kocman and Mrs. L.M. Foley)

ECOLE POLYTECHNIQUE Institut de genie energetique, Montreal, Quebec, Canada (Dr. G. Kennedy and Mr. J. St.-Pierre)

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH Bartow Florida, U.S.A. (Mr. M. Bogan)

GEOLOGICAL SURVEY OF CANADA Ottawa, Ontario, Canada (Dr. C. Gregoire)

MINTEK Randburg, Republic of South Africa (Mr. E.J. Ring)

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TEXAS A & M UNIVERSITY Center for Chemical Characterization and Analysis, College Station, Texas, U.S.A. (Dr. W.D. James)

UNIVERSITY OF ILLINOIS Department of Nuclear Engineering, Urbana, Illinois, U.S.A. (Dr. S. Landsberger)

UNIVERSITY OF MISSOURI Research Reactor Facility, Columbia Missouri, U.S.A. (Dr. M. D. Glascock)

UNITED STATES GYPSUM CORP. Research Center, Libertyville, Illinois, U.S.A. (Mr. J.W. Barber and Dr. B. Hudgens)

WESTDEUTSCHE GIPSWERKE GEBR. KNAUF Iphofen, Fed. Rep. of Germany (Dr. Frantz Wirsching)

X-RAY ASSAY LABORATORIES Don Mills, Ontario, Canada (Mr. P. Boctor)