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OF SOUTH AFRICA

ONDERWERP: IDENTIFICATION OF ZIRCON FROM A DEISTER TABLE CONCENTRATE
SUBJECT: .....

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IDENTIFICATION OF ZIRCON FROM A DEISTER TABLE CONCENTRATE

SYNOPSIS

Zircon, ilmenite and rutile have been identified by X-ray diffraction in a pyrite concentrate prepared from a Witbank coal by means of the Deister Table.

From microscope grain counts, the mass percentage of zirconium in the -125 + 25 µm fraction, is estimated at about 4%.

Research is needed to delineate the occurrence, determine whether the mineral monazite is also present and apply these findings to the utilization of coal wastes.

INTRODUCTION

Zirconium's remarkable refractory properties assure its use in materials subjected to extremely high temperatures, such as in ceramics, refractories, chemical processes, foundry molds and as an alloy. It is also used in atomic energy plants as a moderator and container for pure uranium.

The principal minerals from which zirconium is extracted are baddeleyite (ZrO_2) and zircon ($ZrSiO_4$). Baddeleyite is produced as a by-product from Phalaborwa, though it forms only 0,1%* of the phoscorite. Zircon, though present in trace amounts in many rock types, is generally only recovered as a by-product from ilmenite-rutile-bearing beach sands. In 1969, 100 tons of zircon concentrates from this source were exported at R30 per ton.**

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* P348. Mineral Resources of the Union of South Africa 4th Ed. Government Printer - Pretoria.

** P228. Beerman's All Mining Year Book for 1971. Combined Publishers Johannesburg.

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In this connection it is significant that in a Deister Table concentrate, zircon was found to be a major constituent, after the iron sulphides: pyrite and marcasite.

X-ray data are presented in this report substantiating the identification, quantitative data from grain counts are given and a plea is made for the systematic study of "heavy mineral" concentrates associated with coal.

RESULTS

In October 1974, a pyrite-concentrate was prepared from a Witbank coal by means of the Deister Table at the Institute, with a view to using this material for X-ray calibration purposes. An X-ray diffractometer trace showed the concentrate to be contaminated by marcasite, quartz and an unidentified mineral, (Column 1 Table I) and it was abandoned in favour of better material.

However, in the study of the mineral matter in South African coal, difficulties were experienced with the X-ray identification of minerals present in minor amounts and attention was redirected to the Deister Table concentrate.

A portion of the original concentrate was boiled in 3N HNO_3 in order to remove the iron sulphides and an X-ray diffractometer run was made. The unidentified mineral was clearly zircon (Column 2 Table I) and in addition, ilmenite ($FeTiO_3$) and rutile (TiO_2) were also confirmed. A detailed discussion of the X-ray data (Table I) is given in the appendix.

For further confirmation, sample fractionation by means of a bromoform float and sink separation was attempted. However, no clear demarcation of the float and sink fractions occurred with the coarser particles tending to settle and the finer material tending to remain in suspension to be recovered along with the float fraction. X-ray data show that the "sink" fraction is enriched in zircon (Column 3 Table I) and the "float" fraction contains mainly quartz (Column 4 Table I).

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In order to estimate the amount of zircon present in the concentrate, the sample was sieved into five fractions with reasonably narrow size ranges and grain counts were carried out under a stereomicroscope. Counting was continued to 1000 pyrite grains and because marcasite was not optically distinguishable, it was included with the pyrite. For the -45 µm sieve fraction, only the coarser grains, i.e. +25 µm could be resolved satisfactorily under the microscope and thus be counted.

Since the grains were roughly sized in the sieving operation it was possible to calculate mass percentage data for the minerals (densities used in the calculation are indicated in the Table) and hence for the major elements.

Referring to Table II, zircon is present in all the sieve fractions and is more common than ilmenite in the grain-size range -125 µm to +25 µm. The calculated mass percentage of zircon varies from 7,7 to 9,5% (zirconium 3,8 to 4,7%) in this size range of the Deister Table concentrate.

To test the ease with which ilmenite, rutile and zircon could be recovered, a simple experiment was carried out. The pyrite concentrate in the -125 + 76 µm fraction was roasted in air at 600°C. Pyrite had altered to soft friable hematite (SO_2 could be a possible by-product) which could be freed from the sample by washing in water after it had been mildly ground in a ball mill. Grain counts for the recovered ilmenite, rutile and zircon (counted to 100 zircon grains) are also given in Table II. This roasted concentrate had a calculated zirconium content of 21,4%.

DISCUSSION

Geologically, the association of ilmenite, rutile and zircon is typical of relatively coarse reworked detrital sediments such as in present day beach sands. It is highly unlikely to be present in coal itself or its associated shales and carbonaceous shales, the products of a quiescent environment.

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However, in the mining of coal, sandstone and grit bands from the roof or floor or as partings in the seam may find their way into a consignment of coal. This may have occurred in the present instance, presumably because the coal was not cleaned prior to the Deister Table treatment.

Due to the relatively low pyrite content in South African coals, and for reasons of capacity, Deister Table separators are not incorporated in the standard coal washing plant in the Republic. However, it may be feasible to treat the sinks from a heavy medium bath, or since the refractory nature of the "heavy minerals" (with the exception of pyrite) is well known, treat the ash of unwashed coal, by means of a Deister Table separator or water cyclone, for the recovery of these economically important minerals.

The radio-active mineral, monazite (phosphate of thorium and the rare earths), is a member of the "heavy mineral" suite. Its derivatives are extremely valuable viz. £71505 was paid per pound of thulium in 1957.*** Since monazite is known from the Karroo sediments, it is likely to occur together with zircon, ilmenite and rutile in the "heavy minerals" concentrated from coal.

Clearly more research on the "heavy minerals" associated with coal is needed, and it may make of coal wastes i.e. sinks in the heavy medium bath, or power station ash, an asset, rather than the liability they are at present.

SUMMARY AND CONCLUSIONS

Minerals with economic value such as ilmenite, rutile and zircon have been identified by X-ray diffraction in the pyrite separated from a Witbank coal by means of the Deister Table.

Microscope grain counts established the predominance of zircon, after the iron sulphides, in the grain-size fraction -125 µm to +25 µm with calculated mass percentages of 7,7 to 9,5% and calculated mass percentage of zirconium 3,8 to 4,7%.

*** P287. Mineral Resources of the Union of South Africa 4th Ed. 1959 Government Printer, Pretoria.

Zircon, ilmenite and rutile are easily recovered from the pyrite concentrate by roasting (SO_2 could be reclaimed), gentle milling and washing. The calculated mass percentage of zirconium is increased from 3,8 to 21,4%.

The occurrence of the "heavy mineral" suite in coal is geologically incompatible, but may be due to the inclusion of sandstone and grit bands in coal hauled to the surface.

Further research is required to determine whether the radio-active mineral monazite is also associated with coal, and whether coal wastes are amenable to concentration procedures for the recovery of the economically important "heavy minerals".

ACKNOWLEDGEMENTS

The Deister Table concentrate was prepared under the direction of Mr P J F Fourie, who is also thanked for discussion.

The acid ingestion was carried out by Mr D F Retief under the direction of Mr E F E Müller.

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TABLE II

RESULTS OF GRAIN COUNTS IN SIZED FRACTIONS OF DEISTER TABLE CONCENTRATE

MINERAL	SIEVE FRACTION (µm)					ROASTED* CONC.
	-500 +210	-210 +125	-125 + 76	-76 +45	-45 (+25)**	-125 + 76
No. of grains per 1000 pyrite**** grains:-						
Quartz***	40	8	11	12	-	2
? Apatite	-	3	2	1	-	-
Rutile	-	18	32	18	10	50
Zircon	8	38	100	116	119	100
Ilmenite	30	51	87	71	49	84
Calculated mass % for minerals:-						
Quartz (2,65)*****	2,0	0,4	0,5	0,5	-	0,5
Rutile (4,25)	-	1,4	2,3	1,3	0,7	19,6
Zircon (4,67)	0,7	3,2	7,7	9,1	9,5	43,1
Ilmenite (4,75)	2,7	4,4	6,8	5,6	4,0	36,8
Pyrite**** (5,00)	94,6	90,6	82,7	83,5	85,8	-
Calculated mass % for major elements:-						
Fe	45,1	43,8	41,1	41,0	41,4	13,6
Ti	0,9	2,2	3,5	2,5	1,7	23,4
Zr	0,3	1,6	3,8	4,5	4,7	21,4
S	50,5	48,4	44,2	44,6	45,8	-

NOTES:

* Roasted, milled and washed to remove pyrite. Grains counted to 100 zircon.

** Grains smaller than ca 25 µm ignored in microscope count.

*** Includes quartz intergrown with pyrite.

**** Includes marcasite.

***** S.G. used in the calculation.

APPENDIX: Discussion of X-ray data in Table I

In X-ray diffraction work, use is often made of the so-called "d" - value, given in dimensions of length i.e. Angström (A^o) or 10^{-10} m. This value is obtained from the Bragg relation $n\lambda = 2d\sin\theta$ and gives the spacing between successive identical planes in the crystal structure. Together with their relative intensities, the d-values characterize any crystalline substance.

In a mixture, all the components "diffract" independently of one another, but their diffraction intensities are attenuated by the presence of the other components in the mixture. Use is made of this fact in the identification of the components of a mixture i.e. the strongest diffraction intensities (-lines or -peaks) of a substance must be present on a diffractogram before the weaker diffraction intensities (-lines or -peaks) can be assigned to the same substance for a positive identification.

In Table I, d-values and relative intensities (i.e. intensities on the diffractogram recalculated relative to the strongest intensity equals 100) are compared with the published data on the ASTM card series of the JCPDF. The diffraction lines are numbered and correlated between the four diffractograms.

In Column 1 the diffraction pattern of the original Deister Table concentrate is given. As expected, pyrite contributes to the most intense lines, but the presence of marcasite is indicated by lines 6, 21 and 35 which do not overlap with any pyrite lines. The six strongest lines of the published data for marcasite are thus present. In addition, diffraction peaks of medium intensity occurred at d = 3,334 A^o (line No. 7) and d = 3,293 A^o (line No. 8). The following columns show these lines to be the maxima of quartz and zircon respectively. Ilmenite and rutile's maximum intensities are also present as weak reflections (lines 12, 37 and 9) on the diffractogram of the original sample.

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After treatment with HNO_3, the diffraction lines of the iron sulphide minerals were removed from the pattern and the lines of the acid insoluble minerals were enhanced. In Column 2, the maxima (line No. 8) now correspond to the maxima for zircon, and all the published lines in the angular range to 70° 2θ for cobalt radiation for this mineral, can be matched on the diffractogram. The lines which can be correlated with quartz have increased to five, those of ilmenite to six, and five rutile-lines can be correlated.

The disparity in intensity for the two lines of ilmenite (lines 12 and 37) given as 100 each in the reference, is due to the falling off of intensity towards the higher angular range as a result of geometric factors inherent in diffractometer measurements.

Columns 3 and 4 give results for the sink and float separation of the acid treated material with bromoform. Evidently the separation was unsuccessful, but the relative proportions of the minerals have been altered. The "sinks" are richer in zircon and ilmenite, whilst the "floats" are richer in quartz, some of the weaker lines of the quartz reference data making their appearance on this diffractogram.

Some lines could not be matched. For example, in the acid treated concentrate a substance with a line of relative intensity 10 at d = 3,84 A° was apparently bromoform or alcohol soluble as it is absent from columns 3 and 4. The weak lines 5 and 11 may also not have any significance.