

CALCITE PEAK ANOMALIES IN THE DTA OF OIL SHALES DETERMINED IN FLOWING CARBON DIOXIDE COMPARED TO NITROGEN

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ABSTRACT

The established predictable modifications to the DTA curves of anhydrous carbonate minerals (alone or diluted with inert Al_2O_3), produced in flowing CO_2 compared to N_2 are diagnostically similar when mixed with oil shale with the exception of calcite ($CaCO_3$). The single endothermic calcite peak which, when determined in CO_2 , occurs at a considerably higher temperature, with the same area, in an attenuated form becomes grossly modified when in mixtures with oil shale, i.e., the up-scale peak temperature displacement is greater but the peak size is drastically reduced. This results in much poorer detection limits, provides spuriously low content evaluations and may be obscured or overlooked due to its small size and unexpected peak position.

The commonly accepted exothermic formation of wollastonite ($CaSiO_3$) in this temperature region, which could account by peak superposition for the endothermic calcite peak diminution, could not be substantiated as its presence was not detected by XRD in the DTA residues after heating to $1000^\circ C$. This factor and the alternative explanations considered here in have considerable bearing on oil shale mineralogical effects, retorting technology and heat balances, SO_x retention, and the composition-stability of the spent shale products.

INTRODUCTION

The present work forms part of a continuing study on the thermal analysis effects of natural carbonate minerals and the detailed applications of these minerals to their presence in oil shale and its utilisation. Several related papers have previously been published and are referred to where applicable, but should be consulted in full for many details which are not repeated here [1–5].

Briefly, it has been previously established that the DTA curves of single-reaction anhydrous carbonate minerals determined in flowing CO_2 compared to N_2 result in marked, predictable, reproducible and clearly recognisable peak modifications. Essentially, the increased partial pressure of CO_2 gas

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surrounding the carbonate sample results in a delay in its decomposition reaction.

This then occurs at a diagnostically higher temperature with a more vigorous reaction (the peak moves up-scale). The latter results in an increase in peak height, and attenuation which in turn improves the detection limit [1]. Furthermore, the peak area remains virtually the same for a given content which facilitates comparative carbonate-component proportion evaluations whether determined in CO_2 or N_2 .

However, other inert gases, e.g., He or Ar, cannot be substituted with impunity as peak areas will not be comparable due to their markedly different thermal conductivities [6]. For carbonates which undergo more than one decomposition reaction in CO_2 the peaks not only attenuate but become more widely separated and this separation is maintained down to the limits of detection, i.e., dolomite ($\text{CaMg}(\text{CO}_3)_2$) and ankerite ($\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$) [1,2]. These two minerals are specifically mentioned because their highest endothermic peak occurs in a similar position to that of calcite.

The diagnostically different DTA peak modifications produced for anhydrous carbonate minerals in flowing furnace atmosphere conditions of N_2 compared to CO_2 were detailed in a related recent study [4]. There it was further established that these atmosphere-controlled peak modifications were consistent, with one exception, when produced from artificial mixtures of the individual carbonates with inert Al_2O_3 or low rank oil shale.

The single exception is produced by calcite (CaCO_3) in flowing CO_2 , when present in mixtures with oil shale compared to previous descriptions for mixtures with Al_2O_3 or coal [7]. Whereas in CO_2 compared to N_2 the single endothermic peak of calcite should be displaced up-scale to occur at a considerably higher temperature with the same area but with much increased attenuation [7], in oil shale mixtures it suffers marked modifications. Namely, the up-scale displacement is greater and the peak size as indicated by both its area and height is drastically reduced.

As this phenomenon has serious implications in the areas of detection limits, spuriously low content evaluations, retort heat balance, SO_x complexing-retention, the spent shale product composition and its chemical-thermal stability, it has been investigated further.

Furthermore, due to the unexpected peak-size reduction, the resultant peak may be obscured or overlooked due to its small size and new peak position.

EXPERIMENTAL

Equipment

In all cases the low rank oil shales from deposits in Queensland, Australia were used for the artificial mixtures with calcite. The natural calcite used was

high-purity Iceland spar and all mixtures were prepared on a weight percent basis.

The thermal analysis curves were obtained using a Stanton-Redcroft simultaneous TG/DTA unit (STA 781) under identical experimental conditions to those for the previous study [4].

The XRD examinations were carried out using a Philips PW1700 diffractometer from samples of the residues of the thermal analysis runs which terminated at a minimum of 1000°C.

Semiquantitative analyses were made of grain mounts prepared from the same residues using a Jeol JXA 50A electron microprobe analyser with an Edax 707 energy dispersive X-ray analysis system interfaced to a data Nova 2-10 minicomputer. A program developed by Reed and Ware [8] and modified for this equipment was used to calculate the results. The analytical conditions were: accelerating voltage of 15 kV; specimen current as measured on a standard mount, approximately 1.75 nA; and an electron beam diameter of approximately 0.5 μm .

Samples studied

A series of artificial mixtures was prepared containing one mineral, with or without Al_2O_3 , oil shale with Al_2O_3 and oil shale with various minerals added. The materials were crushed to -200# BSS (-75 μm) and mixed in the correct proportions by weight to give individual 30-mg samples all of which were subjected to DTA in each case. Where duplicate runs were required, an additional 30-mg sample was made up from its individual constituents.

RESULTS

Thermal analysis

In order to clearly delineate these "anomalous" DTA peak modifications obtained for calcite, appropriate curves are presented in Fig. 1, to illustrate the several pertinent features involved. Curves 1 to 4 were obtained from the oil shale with 20% inorganic additive in order to provide DTA curves relatable to commonly occurring oil shales diluted with calcite or inert Al_2O_3 contents of 10 to 20%. Additional curves with 50% calcite added were examined to contrast the effects of high or excessive calcite contents, some examples of which are classifiable as impure limestones [9].

From these and previously published curves in this ongoing investigation it may be seen that:

(1) the oil shale curves (dilutant 20% inert Al_2O_3) are comparable in both N_2 and CO_2 (cf. curves 1 and 2, Fig. 1);

(2) a single, simple endothermic peak represents the decomposition of calcite in either N_2 or CO_2 (see fig. 13 of ref. 7);

(3) this peak, although of comparable area, moves up-scale (higher temperature) and attenuates when determined in CO_2 compared to N_2 (see fig. 13 of ref. 7);

(4) in CO_2 the calcite peak moves up-scale somewhat further, for mixtures of a given amount of calcite, with oil shale, than for calcite with Al_2O_3 ;

(5) the peak size appears reduced by about 90% when determined in CO_2 compared to N_2 (cf. curves 3 and 4, Fig. 1);

(6) the curve from 50% calcite with oil shale in CO_2 compared to N_2 shows a similar peak size reduction of $\sim 90\%$. However, the reduced endothermic

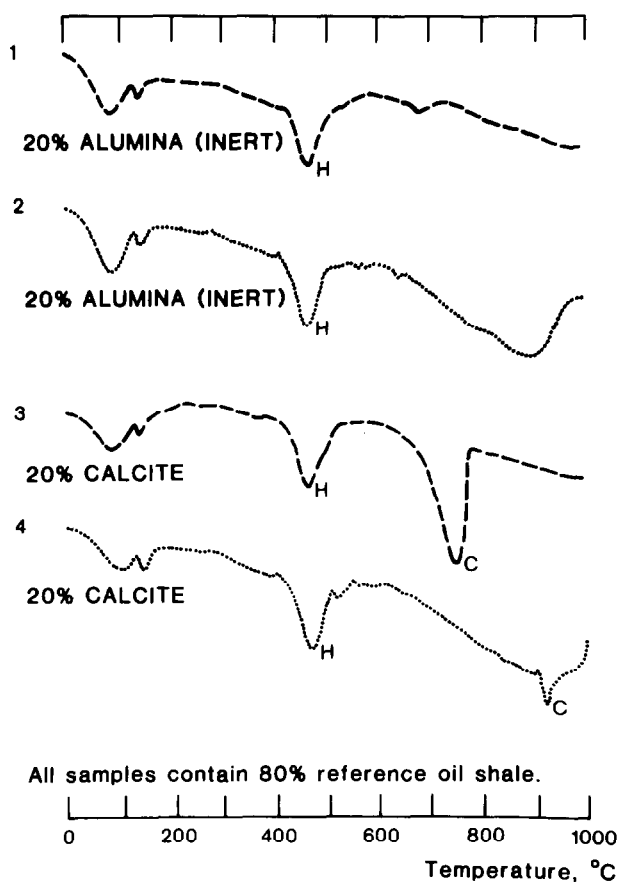


Fig. 1. DTA curves obtained in flowing N_2 (---) and flowing CO_2 (·····) from artificial mixtures as follows: (1) and (2) 80% oil shale with 20% inert Al_2O_3 ; (3) and (4) 80% oil shale with 20% calcite. Oil shale used is from Rundle Queensland. To illustrate the problem of greater up-scale movement and marked peak diminution of calcite when mixed with the same amount of oil shale and determined in CO_2 compared to N_2 . Peaks marked H and C are due to the hydrocarbon yield and calcite, respectively.

effect now shows as three small, closely adjacent endothermic peaks, the highest-temperature one of which is the sharpest.

As some new factor has clearly affected the DTA peak of calcite, the often invoked reaction between calcite and silica minerals (SiO_2) to form wollastonite (CaSiO_3) was considered likely. In this case the exothermic wollastonite-forming reaction which occurs in the same temperature region could be superimposed on the endothermic calcite decomposition peak, reduce its size and be completely negated itself, leaving only a much reduced, residual endothermic peak to represent the original calcite content.

However, high-sensitivity XRD examinations of the solid residues from the calcite/oil shale DTA runs heated to 1000°C failed to detect any wollastonite at all.

In investigations to see if wollastonite would form under these temperature, heating rate and gas atmosphere conditions, artificial mixtures of crushed ($-75\ \mu\text{m}$), mineral calcite and quartz (SiO_2) and laboratory-grade precipitated silica and calcium carbonate were subject to DTA in N_2 and CO_2 . The latter materials were included because of their finer grain size, and increased surface area which would be expected to facilitate reaction. In none of the resultant DTA curves was there evidence of calcite-peak diminution, or wollastonite in the residues.

Additional DTA curves in CO_2 from mixtures of silica and calcite with montmorillonite, and silica and calcite with dolomite were examined in order to establish under what other mineralogical conditions the anomalous calcite peaks would occur.

These two mixtures were used to test if the presence of montmorillonite or dolomite would promote the reaction between silica and calcite to form wollastonite. In both cases, however, the calcite peak remained unaffected.

As the presence of inorganic constituents did not appear to be involved, the role of organic matter was further considered. A mixture of a different oil shale (from Glen Davis, New South Wales) with silica and calcite added was examined. In this case the calcite DTA peak behaved as before, except that the up-scale displacement was $\sim 50\%$ less than for the Rundle oil shale, thus confirming the influence of the organic components.

In order to establish if any CaO was produced under these conditions, cooling curves (in CO_2) were determined from mixtures of 50% calcite with oil shale or Al_2O_3 . In this case the recarbonation peak due to calcite reformation was much less for the oil shale mixture, thus implying that much of the CaO from the calcite decomposition has been otherwise accounted for.

X-ray diffraction and electron microprobe analysis

The complementary XRD and electron microprobe investigations were made on the DTA 1000°C -run residues as determined in CO_2 and N_2 . These revealed a complex series of reaction products some of which could not be

positively identified. However, wollastonite was not detected but portlandite (CaOH_2), together with lesser amounts of calcite and quartz, were identified. Conversely, in N_2 the two dominant minerals detected were portlandite and quartz, together with minor amounts of Ca and CaMg silicates (see details below).

It is noteworthy that re-runs of the same residues showed that the portlandite slowly reverted to calcite over a period of days due to reaction with atmospheric CO_2 .

Further, a sample of CaO, prepared by heating calcite, was repeatedly X-rayed against an inert internal standard, and showed that it reverted to CaCO_3 over a period of several weeks on exposure to air.

Most of the previous pyrolysis studies have been carried out on Green River oil shales, which have very high carbonate and low silicate contents, respectively [10–13]. In contrast, Eastern Australian Tertiary oil shales are dominated by quartz and the clay minerals kaolinite, illite and montmorillonite [2,4,14,15]. Consequently, the Ca and CaMg silicates reported by previous workers [10–13] were not detected. Instead, from our 20% calcite–oil shale mixture residues, complex (Ca, Na and K), (Mg, Fe) alumina silicates resulted, of which members of the osumulite series were identified.

In order to emulate the high-carbonate Green River material a further residue from 50% calcite with oil shale was heated to 1400°C in CO_2 . This could be seen to contain larnite and gehlenite. It would appear therefore that the temperature to which oil shale is heated, and probably the calcite content, influences the composition of the resultant silicates.

It is hoped that these aspects will be pursued further as the need for more detailed information becomes increasingly pertinent for future developments in oil shale retorting technology and spent shale assessment and utilisation.

POSTULATED EXPLANATION OF RESULTS

Under the experimental conditions of this study the formation of wollastonite (or any Ca silicate in large proportions) could not be substantiated. Furthermore, it is clear that the amounts of CaO liberated by the decomposition of calcite for the most part resulted in the exothermic formation of portlandite, which is a major residue constituent. Any remaining CaO would rapidly recarbonate with atmospheric CO_2 as has been shown by the presence of a small calcite recarbonation exothermic peak, originally detailed [16], which shows on the cooling curve of oil shale–calcite mixtures as determined in CO_2 . Furthermore, as described above, the portlandite will also convert, in a short period, to calcite due to carbonation with atmospheric CO_2 .

Also, there appears to be no significant difference in the minor minerals present in these residues.

Thus, the calcite peak anomalies cannot be explained purely in chemical terms.

The work of Burnham et al. [10] furthering previous work [17] may provide an acceptable explanation, i.e., they indicated that carbon of oil coking origin can be produced and deposited by the degradation of liquid oil before it can escape from its point of generation within oil shale fragments during the retorting process.

It could be postulated that at such temperatures this carbon forms in the interstitial spaces, in many cases effectively enclosing or sealing individual small mineral grains, including calcite.

Relevant to this it was noted that all the DTA run residues as determined in N_2 were black and powdery, while those obtained in CO_2 were grey and coherent, and showed signs of minor vesicularity. In the latter case this would imply that the residual carbon is of a somewhat different, and perhaps of a more agglutinating or pervasive nature.

Critical to this concept is the thermal stability of calcite. Thus, although the other carbonate minerals all decompose at lower temperatures, calcite remains unaffected until reaching temperatures considerably above the hydrocarbon yield temperature range for oil shales [4]. This would allow for the deposition of the carbon of organic matter degradation origin. Should this material be capable of effectively sealing the calcite grains, then immediately the calcite decomposition temperature is reached, CO_2 will be produced. Not being able to escape, this would accumulate. As has already been discussed, the increased partial pressure of a surrounding atmosphere of CO_2 delays the calcite decomposition reaction. Should this CO_2 pressure be contained so as to build up above ambient, the calcite decomposition would be delayed still further than in flowing CO_2 at ambient pressure. This is exactly what has been observed in the present study, i.e., an even further up-scale movement of the calcite decomposition peak when present with the oil shale, compared to Al_2O_3 in CO_2 .

It could be envisaged that before too long the "seal" would be penetrated, the CO_2 pressure drop and the calcite immediately decompose.

At the same time the immediate availability of H_2O as steam (an important constituent of oil shale) could rapidly ensure that the CaO would be immediately slaked to form portlandite. As this reaction is exothermic and rapid it would account by peak superposition for the marked size reduction of the endothermic decomposition peak of calcite.

That this only happens under DTA in CO_2 could be attributed to the delay in the decomposition of the exposed calcite grains until they are sealed by the deposition of the carbon product.

The question could also be asked: why the high temperature peak of dolomite or ankerite, which in general terms may be considered as due to the decomposition of the " $CaCO_3$ " component, is not affected in the same way as calcite?

Previous work clearly demonstrated that in CO_2 the earliest decomposition peak occurs at lower temperatures [7] which fall progressively with increasing Fe content [2]. Thus, in the related study [4] as these down-scale peak displacements for 20% mixtures of dolomite and ankerite with oil shale are as expected, it is clear that any potential "carbon sealing" is negated by these lower-temperature decompositions and their associated vigorous CO_2 evolution.

DISCUSSION AND CONCLUSIONS

When determined in furnace atmosphere conditions of CO_2 compared to N_2 , calcite present with the oil shales studied shows a marked reduction in the size of its characteristic endothermic DTA peak (about 90%) and an unexpectedly large up-scale displacement, i.e., it occurs at an even higher temperature than the same amount of calcite when mixed with Al_2O_3 .

These two features, once documented, are of diagnostic value as the common oil shale anhydrous carbonates siderite, magnesite, dolomite and ankerite are not similarly affected at all.

The reduction of the calcite peak to about 10% of its original size must be taken into careful account in relation to calcite detection limits, content evaluation and the greatly reduced amount of heat required from the retorting system during the calcite decomposition.

The formation of portlandite is strongly exothermic and thus assists in maintaining the required retorting temperature and reduces costs.

Calcite-derived wollastonite or other Ca or CaMg silicates in the spent shale would be chemically and physically stable. Alternatively, portlandite and any residual CaO present will react exothermically with atmospheric CO_2 at NTP to form CaCO_3 . In this way some spent shale dump self-generated heat may be expected and its effects on large dumps of such carbon-rich waste is a factor for consideration. Also, mineral formation is often physically disruptive. This may lead to reduced particle size and the unwanted production of fines.

Conversely, such alkaline material could well be of value as a neutralising agent if interlayered in dumps with acidic materials, i.e., pre-retorting beneficiation oil-shale refuse containing pyrite-derived acid leachates. This is a role for which fly ash has also been used as well as for a soil conditioner in agriculture.

Finally, alkaline compared to acid waste dump environments are less likely to release heavy metals into the immediately adjacent environment.

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