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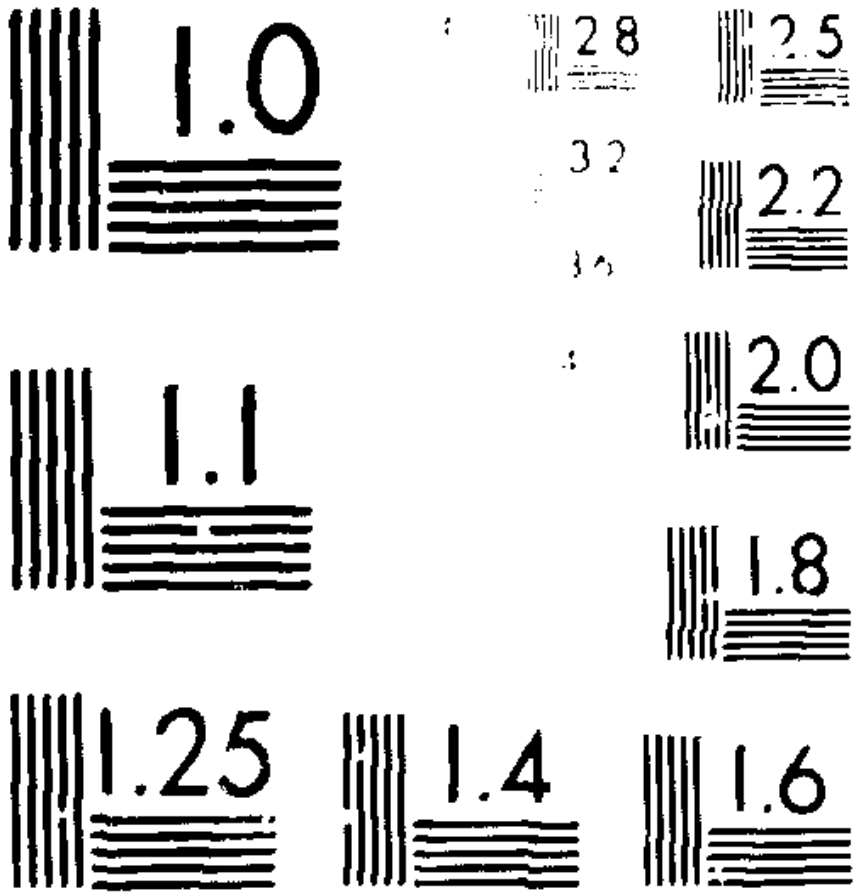
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→ Maria Dietrich

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# LIMESTONE SAMPLES FROM ANTIGUA

## Chemical Analyses

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I. ABSTRACT

This report concerns itself with an evaluation of 2 limestones from Antigua Island with special regard to the use of these limestones for agricultural and industrial purposes. The analyses also anticipate the quality of burnt lime and hydrate.

Both limestones may be applied in lime and hydrated lime manufacture. Seaforth limestone sample A is of a better quality and, therefore, more appropriate for lime burning.

Limestones themselves are suitable for many industrial and agricultural purposes.

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## III. INTRODUCTION

Two samples from Antigua Island were delivered to the UNIDO-CSSR Joint Programme late in March 1981. The samples were accompanied by a letter of the East Caribbean Common Market Secretariat No. 03/00/03 dated 24 February 1981 and signed by Mr. Neville R. Hill, UNIDO Building Materials Geologist, with reference to UNIDO/ECCM Secretariat Project CAR/73/001. The letter was addressed to the Liaison Officer of the UNIDO-CSSR Joint Programme, Industrial Operations Division, UNIDO Vienna.

Definition of Samples:

The delivered samples are as follows:

Sample No. 140281 A

Location: Seaforth, grid No. 194905
Grid reference refers to the 1977 edition of the 1:50,000 scale map of Antigua (Ref. No. VI/2)

Site of Sample: From surface outcrop of rock at about [illegible]0 places on the top and West side of [illegible] hill.

Sample No. 140 [illegible]

Location: Willis Freeman, grid No. 320841
(Ref. No. VI/2)

Site of Sample: Surface outcrop in clearing in uncultivated vegetation. 1/2 km WSW of Goat Hill, pieces chipped from about 15 points on the outcrop

A sufficient quantity of samples has been delivered to carry out complete chemical analyses the results of which are being presented.

The sedimentary limestone sample of Seaforth is pale grey, sometimes buff coloured, hard, compact, otherwise fine grained and uniform. (Ref. No. 1)

The Willis Freeman limestone is pale grey-brown, fine grained, hard, compact and uniform. (Ref. No. 1)

## IV. CONCLUSIONS AND RECOMMENDATIONS

On the basis of the analyses of limestones from Central Plain of Antigua - samples Seaforth No. 140281 A and Willis Freeman No. 140281 B - the following conclusions have been made:

1. Both limestones are suitable for the manufacture of lime and for other purposes.

2. Seaforth limestone is of a better quality and, therefore, for lime burning more appropriate.

3. The analyses confirm the correctness of orientation in exploration carried out by UNIDO experts in this regions.

4. Experimental burning is recommended to be done in order to evaluate the behaviour of limestone in burning process and to define the properties of lime. For this purpose approx. 50 kg of representative samples in lumps at least 125 mm in size are needed. These samples would serve for making test cubes for pressure resistence test before and after burning, hydration tests and quality tests of lime and hydrate.

5. Since chemical analyses show that industrial exploitation of both limestones is feasible, it is recommended to carry out the detailed geological evaluation in order to determine the quantity as well

as possible fluctuation of limestone quality in both deposits.

6. Seaforth limestone No. 140281 A is suitable for the manufacture of Portland cement, quick and hydrated lime and for other purposes, e. g. for the manufacture of colourless sheet glass, semi-white and coloured glass, for pulp industry, coal mine dusting, waste acids neutralization, asphalt filler, masonry cement, for the manufacture of ceramic pottery, mineral wool, fertilizers, paperboard filler, linseed oil, putty for carpentry and windows glazing, asphalt roofing material and poultry grits. The lime is suitable for the manufacture of sand-lime bricks for construction and soil stabilization.

7. Willis Freeman limestone No. 140281 B is suitable for the manufacture of Portland cement, quick and hydrated lime. Limestone itself is suitable for semi-white and coloured glass and bottles manufacture, for the waste acids neutralization, as an asphalt filler, for the masonry cement, mineral wool and fertilizer production, for the linseed oil putty, asphalt roofing material and poultry grits manufacture. The lime could be used for the manufacture of sand-lime bricks, for the hydrated lime and for construction and soil stabilization.

## V. TESTING AND EVALUATION OF LIMESTONE SAMPLES

### 1. Description of Supplied Limestone Samples

The two samples do not differ in aspect and colour.

The sedimentary limestone sample of Seaforth is pale grey, sometimes buff coloured, hard, compact, fine grained and uniform.

The Willis Freeman limestone sample is pale grey-brown, fine grained, hard, compact and uniform.

### 2. Evaluation of Supplied Limestone Samples

Detailed chemical analyses have been carried out regarding the samples of limestone Seaforth No. 140281 A and Willis Freeman No. 140281 B with the following results:

Table No. 1 Chemical Analyses of Limestone Samples from Antigua Island

| | Seaforth No. 140281 A | W.Freeman No. 140281 B |
|---|---|---|
| $SiO_2$ | 4.87 % | 7.71 % |
| $Al_2O_3$ | 0.10 | 0.82 |
| $Fe_2O_3$ | 0.10 | 0.38 |
| $TiO_2$ | 0.02 | 0.05 |
| $P_2O_5$ | 0.02 | 0.10 |
| CaO | 52.03 | 49.75 |
| MgO | 0.89 | 0.56 |
| $CO_2$ | 41.57 | 39.63 |
| $SO_3$ | 0.01 | 0.01 |
| MnO | 0.12 | 0.34 |
| $K_2O$ | 0.01 | 0.15 |
| $Na_2O$ | 0.07 | 0.27 |
| | 99.81 % | 99.77 % |

Assuming CaO and MgO to be bound exclusively in the carbonates, we can deduce the theoretical content of $CO_2$ in the raw meal:

| | Sample A | Sample B |
|---|---|---|
| $CO_2$ determined by chemical analysis, % | 41.57 | 39.63 |
| $CO_2$ figured out of the carbonates, % | 41.80 | 39.66 |

The closeness of these two figures indicates quite clearly that CaO and MgO are present in the samples in the form of carbonates and hence the $SiO_2$ occurs primarily as free quartz sand.

The chemical analyses show that the limestones have slightly increased $SiO_2$ content, in particular as regards the sample B.

The conversion of calcium oxide and magnesium oxide to calcium carbonate and magnesium carbonate results in the following content of carbonates:

| | Seaforth 140281 A | Willis Freeman 140281 B |
|---|---|---|
| $CaCO_3$, % | 92.87 | 88.80 |
| $MgCO_3$, % | 1.86 | 1.17 |
| Total carbonates, % | 94.73 | 89.97 |

## Evaluation of Antigua Limestones for Industrial, Agricultural and Other Purposes and for the Manufacture of Lime

### Manufacture of Portland cement

Both samples are suitable for the manufacture of Portland cement. The increased content of $SiO_2$ is not detrimental provided that the argillaceous component has a lower $SiO_2$ level which as a rule does not pose a major problem.

In view of an elevated content of manganese oxide in both samples, they are not suitable for the manufacture of white cement.

Should these limestones be considered for the manufacture of Portland cement in kiln systems with suspension counter-current preheaters, it would be necessary to check the content of chlorides in a larger number of samples. The Cl content should not exceed 0.02%.

### Production of natural hydraulic lime

In order to assess the hydraulic properties on the basis of chemical analysis, generally the following formulas are used:

a) Michaelis' hydraulic modulus

$$M_h = \frac{CaO}{SiO_2+Al_2O_3+Fe_2O_3}$$

b) Leduc-Le Chatelier-Deforge

$$\frac{SiO_2+Al_2O_3+Fe_2O_3}{CaO}$$

c) Cementation Index

$$\frac{2.8\ SiO_2\ \% + 1.1\ Al_2O_3\ \% + 0.7\ Fe_2O_3\ \%}{\%\ CaO + 1.4\ \%\ MgO}$$

d) Formula of Vicat-Durand-Clay $\frac{SiO_2 + Al_2O_3}{CaO}$

| Formula | Limestone A | Limestone B |
|---|---|---|
| a) | 9.98 not hydraulic | 5.35 moderately hydraulic |
| b) | 0.10 not hydraulic | 0.187 moderately hydraulic |
| c) | 0.265 - " - | 0.45 - " - |
| d) | 0.095 - " - | 0.163 - " - |

Conclusion

Limestone A cannot be burned to hydraulic lime since it does not contain sufficient quantities of hydraulic components. These, however, are present in

limestone B in increased levels of silica components and that's why this limestone can be (from the point of view of chemical composition) brandad as moderately hydraulic.

Regarding the quality of the hydraulic lime produced, the final evaluation cannot be made until the experimental burning has been performed. However, the peak quality would never be obtained.

Since the interest in hydraulic lime is generally on a decline, the outlook for this product should be given the most serious study and considerations.

Table No. 2 **Various Uses of Limestones A and B on Comminution (Crushing, Grinding)**

Limestone Samples, Antigua

| | Limestone A - Seaforth | | Limestone B - Willis Freeman | |
|---|---|---|---|---|
| | Suitability | Reason | Suitability | Reason |
| **Glassworks** | | | | |
| - optical glass | not suitable | high $Fe_2O_3$ content | not suitable | very high $Fe_2O_3$ content |
| - crystal glass | less suitable | higher $Fe_2O_3$ content | not suitable | very high $Fe_2O_3$ content |
| - colourless sheet glass | suitable | | less suitable | |
| - semi-white and coloured glass, bottles | suitable | | suitable | |
| **Pulp industry** | suitable | | not suitable | high $Fe_2O_3$ and $SiO_2$ contents |
| **Industry of viscose cellulose** | less suitable | higher $SiO_2$ content | not suitable | high $Fe_2O_3$ and $SiO_2$ contents |
| **Coal-mine dusting** | suitable | | less suitable | higher $SiO_2$ content |
| **Waste acids neutralization** | suitable | | suitable | |
| **Neutralisation of acids in chemical industry** | less suitable | high $SiO_2$ content | not suitable | high $Fe_2O_3$, MnO and $SiO_2$ contents |
| **Soda ash manufacture** | less suitable | high $SiO_2$ content | not suitable | high $Fe_2O_3$, MnO and $SiO_2$ contents |
| **Rubber plants** | not suitable | high MnO and $SiO_2$ contents | not suitable | high MnO and $SiO_2$ contents |

to be continued

Table No. 2 - Continuation

| | |
|---|---|
| Masonry cement | suitable |
| Manufacture of glass | not suitable |
| Manufacture of ceramic pottery | suitable |
| Mineral wool | suitable |
| Fertilizers | suitable |
| Paperboard filler | suitable |
| Cosmetics | necessary to |
| Manufacture of cables | not suitable |
| Self-fluxing sinters of iron ore | mostly less suitable |
| Linseed oil putty for carpentry and window glazing | suitable |
| Asphalt roofing material | suitable |
| White pigment filler and pigment extender | less suitable |

to be continued

| | | |
|---|---|---|
| | suitable | |
| high MnO content | not suitable | high MnO content |
| | less suitable | higher $Fe_2O_3$ and MnO contents |
| | suitable | |
| | suitable | |
| | less suitable | high $SiO_2$ content |
| test the whiteness of very finely ground sample | | |
| high MnO content | not suitable | high MnO content |
| high $SiO_2$ content | not suitable | high $SiO_2$ content |
| | suitable | |
| | suitable | |
| | not suitable | high $Fe_2O_3$ and MnO contents |

Manufacture of lime

In order to evaluate the samples regarding the production of lime, first of all the composition of burned samples had to be defined, and further the chemical composition of lime produced from these samples.

Table No. 3 Measured Lime Composition /%/

| | Sample A | | Sample B | |
|---|---|---|---|---|
| | comp. of burned sample | measured comp. of lime | comp. of burned sample | measured comp. of lime |
| $SiO_2$ | 8.35 | 8.18 | 12.80 | 12.54 |
| $Al_2O_3$ | 0.17 | 0.17 | 1.36 | 1.36 |
| $Fe_2O_3$ | 0.17 | 0.17 | 0.63 | 0.62 |
| $TiO_2$ | 0.03 | 0.03 | 0.08 | 0.08 |
| $P_2O_5$ | 0.03 | 0.03 | 0.17 | 0.17 |
| CaO | 89.22 | 87.44 | 82.60 | 80.95 |
| MgO | 1.53 | 1.50 | 0.93 | 0.91 |
| $CO_2$ | 0.00 | 2.00 | 0.00 | 2.00 |
| $SO_3$ | 0.02 | 0.02 | 0.02 | 0.02 |
| MnO | 0.21 | 0.21 | 0.56 | 0.55 |
| $K_2O$ | 0.02 | 0.02 | 0.25 | 0.24 |
| $Na_2O$ | 0.12 | 0.12 | 0.45 | 0.44 |
| | 99.87 | 99.89 | 99.85 | 99.85 |

Table No. 4 Various Uses of Lime Produced from Limestones A and B

Limestones Samples, Antigua

| | Lime A (Seaforth No.140281 A) | | Lime B (Willis Freeman No. 140281 B) | |
|---|---|---|---|---|
| | Suitability | Reason | Suitability | Reason |
| Manufacture of sand-lime bricks | suitable | | suitable | |
| Manufacture of calcium carbide | not suitable | high $SiO_2$ and $P_2O_5$ contents | not suitable | very high $SiO_2$ and $P_2O_5$ contents |
| Construction purposes (lumps) | suitable | | suitable | |
| Construction lime (pulverised) | suitable | | suitable | |
| Manufacture of hydrated lime | suitable | | suitable | +/ |
| lime for sugar mills | less suitable | high $SiO_2$ and MnO content | not suitable | high $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and alkalis contents |
| Manufacture of nitrogen fertilisers | not suitable | high $SiO_2$ and MnO contents | not suitable | high $SiO_2$, $Fe_2O_3$, and MnO contents |

to be continued

+/ Higher rejects volume by hydration but high quality product could be achieved.

Table No. 4 - Continuation

| | | | | |
|---|---|---|---|---|
| Pig iron | less suitable | rather high $SiO_2$ content | not suitable | very high $SiO_2$ content |
| Steel manufacture | not suitable | high $SiO_2$ content | not suitable | high $SiO_2$ content |
| Soil stabilisation | suitable | | suitable | |
| Manufacture of ferro-alloys | less suitable | rather high $SiO_2$ and low CaO contents | not suitable | very high $Al_2O_3$, $Fe_2O_3$ and $P_2O_5$ contents |

## VI. FINAL NOTE

Laboratory tests of two samples of Antigua Central Plain origin approved their applicability for industrial and agricultural utilization. However, the final geological evaluation should be done before the elaboration of the feasibility report.

Burning tests should be carried out in order to prove mechanical and physical properties of raw limestone and burnt lime.

Both limestones from Antigua are valuable for industrial enterprise.

## VI. REFERENCES

1. East Caribbean Common Market Secretariat's letter of 24 February 1981, signed by Mr. Neville H. Hill, UNIDO Building Materials Geologist, sent to the Liaison Officer of the UNIDO-CSSR Joint Programme, Industrial Operations Division, UNIDO Vienna

2. Scale map of Antigua, 1977 edition, scale 1:50,000

3. Research Institute of Building Materials in Brno, letter Ref. 64-Ing. Vo/K, dated 14 May 1981 - Report on chemical analyses of 2 Antigua samples