MAKING CEMENTS

WITH

PLANT EXTRACTS

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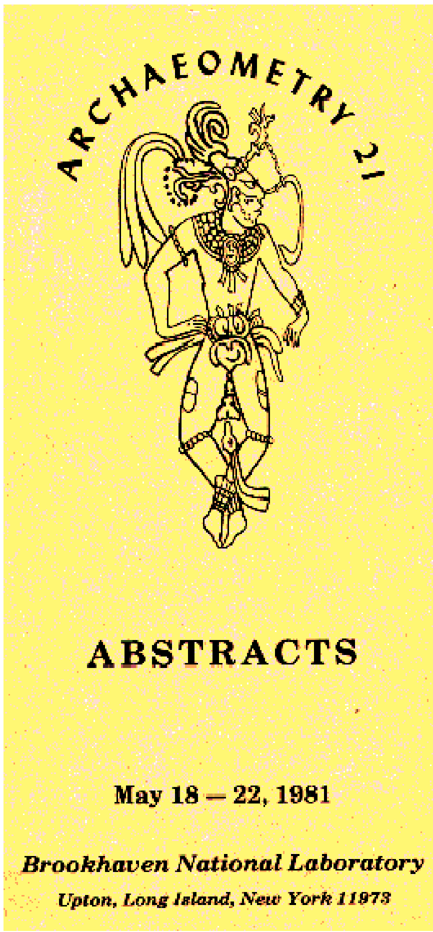

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Abstract of the paper presented at the 21st International Symposium for Archaeometry Brookhaven National Laboratory, New-York, USA, 1981, page 21

FABRICATION OF STONE OBJECTS, BY GEOPOLYMERIC SYNTHESIS, IN THE PRE-INCAN HUANKA CIVILISATION (PERU)

by
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It is now agreed, that the TIHUANACO civilisation is modeled on the pre-incan HUANKA civilisation revealed by an extraordinary skill in fabricating objects in stone.A recent ethnological discovery shows that some witch-doctors in the HUANKA tradition, use no tools to make their little stone objects, but still use a chemical dissolution of the stone material by plant extracts. The starting stone material (silicate or silico-aluminate) is dissolved by the organic extracts, and the viscous slurry is then poured into a mould where it hardens. Already known are examples of fabrication of objects in hard stone by moulding a geopolymeric compound of the Na-,K-poly(sialate)(silico-oxo-aluminate) type. In this case, alcaline mineral reactants such as alcaline frit, caustic soda, soda (the Natron salt of the ancient egyptians) are used (l).On the other hand , in the case of pre-incan HUANKA civilisation, the geopolymeric reaction takes place through organo-mineral complexes as intermediate (plants).These chemical mechanism are known in geochemical, mineralogical, and geopolymeric sciences, especially in certain synthesis of zeolithic type poly(sialates) (2).

The organo-mineral complexes are obtained through the intermediary of oxalates, tartrates, succinates, fulvates, etc. . (3). It is known also that the organo-mineral complexes have a very strong dissolving action on the natural silico-aluminates (feldspar, hornblende, laterite, chlorite,...), their dissolving action being 2 3 times greater than that of sulphuric acid or hydrochloric acid (4). The most highly activ organo-mineral complexes are those obtained with oxalic acid, which is found in large quantities in numerous plants (5). Statues which could have been made by the technique of the pre-incan HUANKA, by dissolution followed by geopolymeric agglomeration, are found to contain Ca-oxalate in the stone (6).

This technique, when mastered, allows a sort of cement to be made by dissolving rocks; this chemical cement then serves to agglomerate aggregates or/and sands. The geopolymers obtained by these organo-mineral synthesis methods are either of the zeolithic, feldspathoidic or amphibolic type.

The technique of the HUANKA people is illustrated by numerous objects found in the CUZCO site. Stone objects made with this technology all bear marks indicating that moulding has been used.

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THE DISAGGREGATION OF STONE MATERIALS WITH ORGANIC ACIDS FROM PLANT EXTRACTS, AN ANCIENT AND UNIVERSAL TECHNIQUE

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At the XXI° Archaeometry Symposium (1), we presented the hypothesis that the large stones in precolumbian monuments were artificial, having been agglomerated with a binder obtained by disaggregating certain rocks (in agreement with local legend and tradition) .

We present here the first results on plant extracts on the dissolution or disaggregation of calcium carbonate containing rocks (Bio-tooling action). The feasibility of chemically working calcium carbonate with strong acids (hydrochloric and formic acid) and various carboxylic acids found in plants (acetic, oxalic and citric acid) has been studied.

Experimental

The calcium carbonate used was from a homogeneous local deposit, broken into lumps. The technique was to scrape a depression in the surface, 2 cm diameter and 0.2 cm deep, then to add 0.5 ml of the acid solution. This was then worked with a flexible plastic spatula chosen to reduce scraping action. The resulting paste was removed when action appeared to have ceased. A furtner 0.5 ml each of acid was added and the process repeated until a total of eight additions of 0.5 ml each of acid has been made, i.e 4 ml in all. The volume of the resulting hole Vh was then measured. The scraping action of the «tool» was measured using pure water (eight additions of 0.5 ml each, i.e 4 ml in total). The volume of the resulting hole Vh was 3.5 ml. Without water, (i.e dry), the volume of the hole scraped during the same time (about 15 minutes) was 0.7 ml. The aim was to carry out a quantitative investigation while at the same time trying to use conditions where scraping action of the «tool» was minimized. It was for this reason that we chose to work with a plastic spatula (polyethylen) and to remove the paste progressively. It is obvious that working with hard «tools» increases the yield considerably.

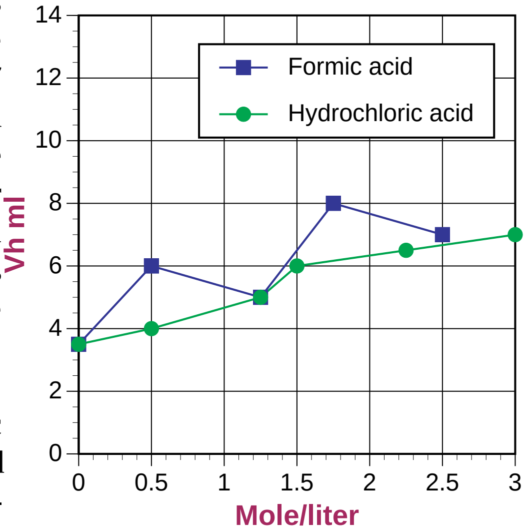


Figure 1: Volume Vh obtained with Formic and Hydrochloric acids

The action of strong acid solutions in water (formic and hydrochloric acid) is weaker than generally expected (Fig.1). There is no increase in the disaggregation at concentrations higher than 2 moles/liter. Acetic acid (Fig. 2) shows a better «bio-tooling» effect. Acetic acid is a major component of natural vinegar (1M to 2M concentration).

Oxalic acid (Fig. 3) forms an insoluble, very hard, calcium oxalate, which precipitates and hinders the bio-tooling action. Citric acid (Fig.3) shows a maximum between 1 M and 1.5 M concentration. The slowing down with higher concentrations is due to reduced dissociation of the acid. Citric acid is present in large quantities in citrus fruits (1 M citric acid concentration), and in the sap of the succulent plants: Agave, Opuntia.

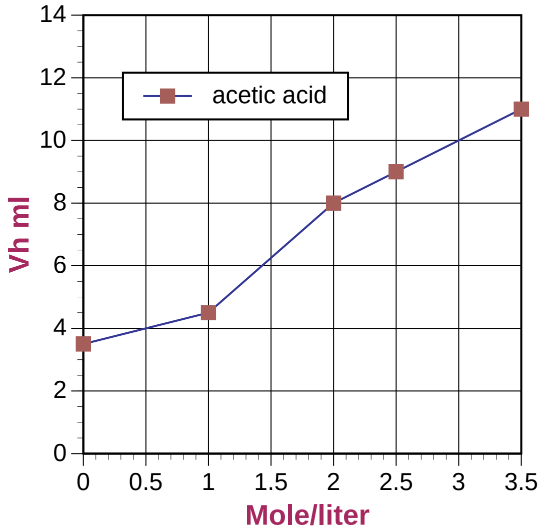


Figure 2: Volume Vh obtained with Acetic acid (vinegar)

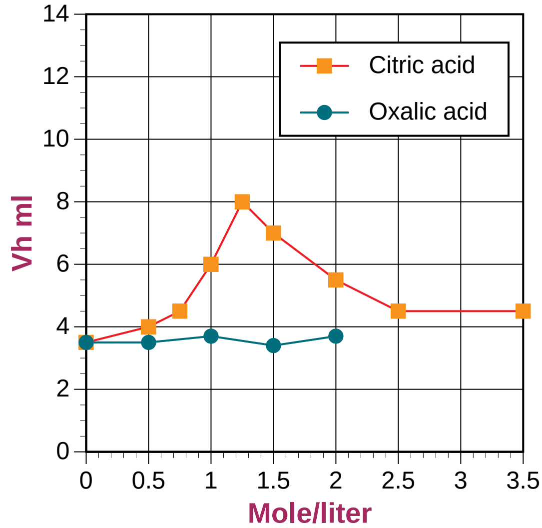


Figure 3: Volume Vh obtained with Citric and Oxalic acids

With addition of oxalic acid to vinegar (1 M) (Fig. 4) maximum rate of dissolution is reached after which at higher concentration of oxalic acid, apart from slowing down due to reduced dissociation of the acid, the calcium oxalate precipitates and hinders the action. Addition of citric acid improves the yield (Fig.4), which apart from its own dissolution action, forms a soluble complex with the calcium oxalate and renders the oxalic acid more efficient for the disaggregation. Maximum bio-tooling action is obtained with a solution containing:

- vinegar (1 M) (acetic acid)
- oxalic acid (0.9 M)
- citric acid (0.78 M)

Addition of formic acid (Fig.5) slows down the action of citric acid. The high pH of the solution reduces the dissociation of the acids, and consequently the «bio-tooling» effect.

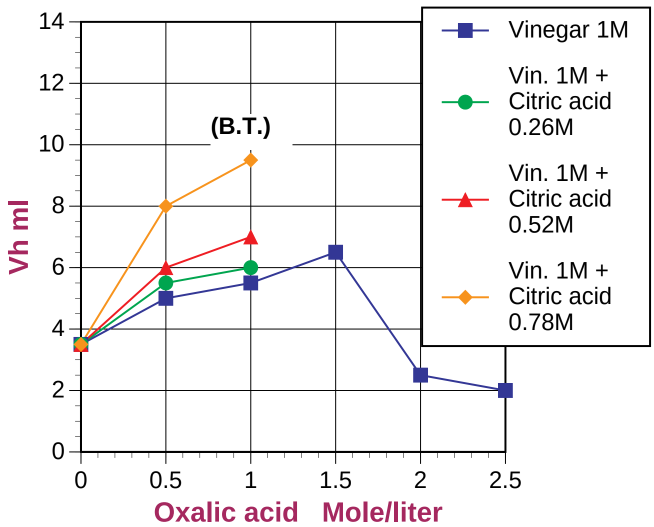


Figure 4: Volume Vh obtained with a solution of Vinegar 1M acetic acid containing Citric and Oxalic acids

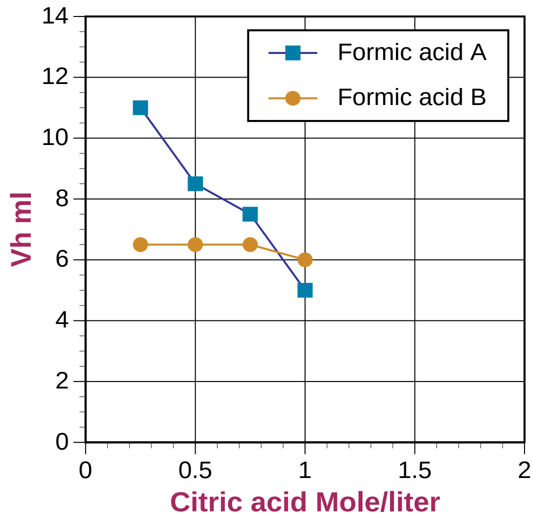


Figure 5: Volume Vh obtained with solutions of Formic acid 0.5 M containing: (A): Citric acid , Vinegar 1M, Oxalic acid 1.2M; (B): Citric acid , Vinegar 1M, Oxalic acid 0.4M

In parallel with these experiments, we have chromatographically identified acids found in various plants and we shall repeat the above experiment with actual plant extracts, basing our choice of plant extract mixtures on the best results obtained above (Table 1).

Table 1: identification of carboxylic acid in various plants

Plants \ Acids	Acetic	Glycolic	Glyoxylic	Propionic	Lactic	Pyruvic	Glyceric	Butyric	Valeric	Oxalic	Tartaric	Succinic	Fumaric	Malic	Citric	Ascorbic	Formic
Bourse à Pasteur Capsella Bursapastoris	xx													xx	xx		
Blackberry Bush Rubus Fructicosus					xx					xx		xx		xxx			
Olive Tree Olea Europea		xx			xx						x			xx			
Nettle Urtica Dioixa										x							xx
Patience Dock Rumex Crispus										xxxx							
Opuntia O. Ficus Indica										xx	xx			xx	xxx	x	
Sorrel Rumex Acetosa										xxxx							
Agave Agave Corulescens														xxx	xx	x	
Agave Americana Variete Marginata											x			x	xxxx	x	

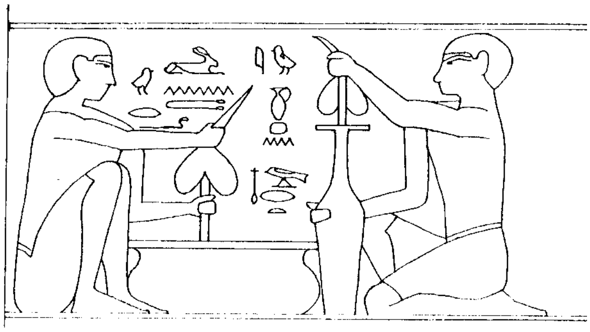
abundance								
	x	low	xx	medium	xxx	high	xxxx	major

Discussion

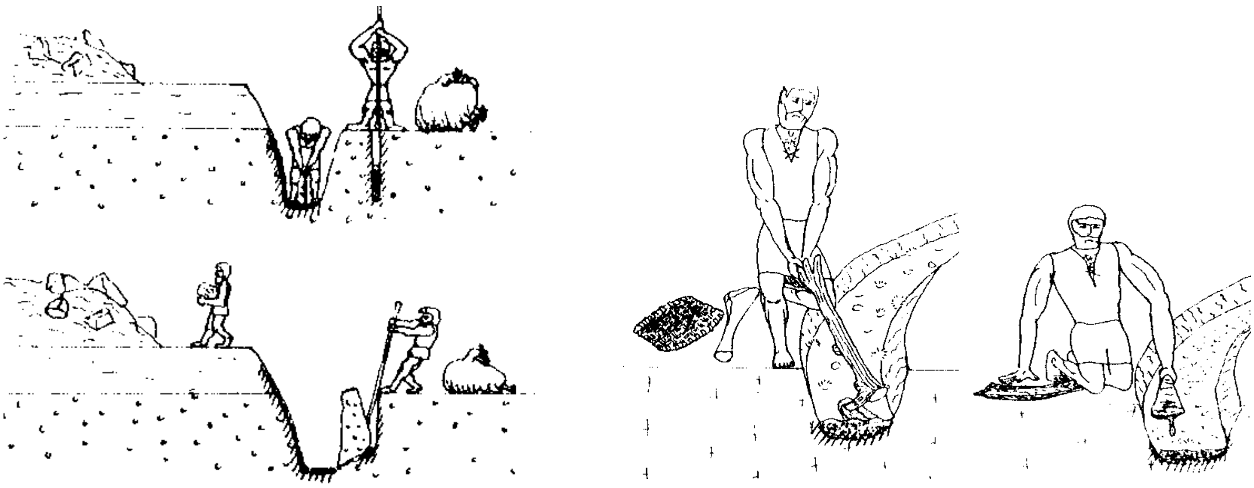
Acetic acid can easily be made in industrial quantities. The simple fermentation of sugar, from fruits, plants and roots, has been used in Antiquity to produce enormous quantities of vinegar (1 M and 2 M) (acetic acid concentration).

The great surprise was actually to discover very ancient references to their use since Neolithic times for working materials which are very hard but easily attacked by acids, such as chalk. Thus, a bas-relief from the tomb of Mera, at SAQQARAH (VI° dynasty, 3°Millenium B.C., Egypt) (Fig.6) shows the hollowing out of «Egyptian alabaster» ($CaCO_3$) vases by a liquid contained in a water skin or bladder.

Figure 6: A bas-relief from the tomb of Merah at Saqqarah (VI° Dynasty, 3° Millenium B.C.), Egypt, shows the hollowing out of "Egyptian alabaster" ($CaCO_3$) vases by a liquid contained in a water skin or bladder.. Hieroglyphic text: *wni 'trf i'w pn nwrt* (It is for thee Ouni, this vessel is the greatest).



PLINY (2) mentions the use of vinegar (acetic acid) in the disaggregation of limestone rocks, and HANNIBAL (219 B.C.) is known to have used the technique to bore holes in, and burst open rocks obstructing his path through the Alps, in his attempt to conquer ROME. We may suppose this technique to have been used in part for the Avebury circle ditch (U.K.), for «The ditch... a floor so smooth.. so well cut... no toolmarks on the walls, vertical and smooth faces.. the finest example of cut chalk.. .the hardest chalk must have been loosened...»(3) (Fig.7 and Fig. 8).



Figures 7/8: The work in hard chalk with antler-, bone- and wood- tools, with the aid of vinegar/rumex extract. We may suppose this technique to have been used in part for the Avebury Circle Ditch (U.K.), for: *"The ditch.. a floor so smooth ... walls so well cut ... no toolmarks on the walls, vertical and smooth faces .. the finest example of cut chalk .. the hardest chalk must have been loosened ..."* (3).

The aliphatic dicarboxilic acids (oxalic, tartaric, succinic,) have a more specialised used in the formation of organo-mineral complexes necessary for certain geopolymerisations. Oxalic acid already belongs with ancient metallurgical techniques universally used: Corinthian Bronze (4) , Precolumbian gilding, Japanese Shaku-do. Oxalic acid in the free state is only found in small quantities in the plants: rhubarb, sloe, sorrel (rumex), oxalis-pubescens, etc..., since these plants contain mainly the salt calcium oxalate, which has to be transformed into oxalic acid. To do this, another organic acid is used: citric acid, present in large quantities in citrus fruits and as up to 70% of the sap of such succulent plants as: Opuntia Ficus Indica, Agave Americana, plants found in great profusion in the mediterranean countries, Australia, and N. and S. America. When sorrel (rumex) is mixed with the sap of Opuntia, the citric acid in the opuntia shifts the oxalate equilibrium in the sorrel towards oxalic acid; thus is obtained an important mixture of acids: oxalic, citric, tartaric, malic, formic...

The precolumbian farmers were quite capable of producing large quantities of acids from such common plants in their region as:

> fruits, potatoes, maize, rhubarb, rumex, agave americana, opuntia, ficus indica, oxalis pubescens.

An experiment of interest was to compare the «bio-tooling» technique with the shaping of a hole using steel tool and the quartz sand technique recommended by prehistorians. The test was run for 15 minutes and the Vh measured for each technique.

Vh after 15 minutes of working	
steel tool	12 ml (spoon spatula)
quartz sand	8.5 ml
bio-tooling (point B.T.) on Figure 4	9.5 ml

The hole resulting from sand abrasion has rough walls, whereas bio-tooling gives a smooth finish.

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