The Effect of Additives
on the
High Temperature Chemistry
of
Investment Materials

by
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Work with additives that quickly remove carbon from
investment molds could reduce energy costs and how these
additives effect the strength of the investment.
Measurements of investment strength and permeability at
casting temperature are reported. The effect of expansion
and contraction of investment on mold filling is discussed.
The reactions and reaction temperatures of calcium sulfate,
plaster of paris, gypsum, quartz, cristobalite and carbon are
given from references and experiments.

Investment

A newspaper article during World War II reported that a long lost metal casting method had been rediscovered and this was very useful in the war effort. It was called the Lost Wax method. Of course this really means the wax is lost not the method. In my later self-education of jewelry making the books I read referred to centrifugal lost wax casting as the invention of a dentist in Louisiana. In a recent search I found that many dentists independently and at about the same time both here and in England were developing wax casting methods.

I have no information about the development of the investment material used for dental lost wax casting. It seems reasonable that plaster of paris, surely well known to dentists, was an early casting material. In any case by the time that jewelers started casting, dental investment and methods were well established.

In my early days of learning jewelry making I attended casting workshops in Dallas. There I met an executive of Kerr who in his younger days had been a Kerr salesman. His area included New York City. One day he was called into the home office and told that he was wasting time calling on jewelers - investment was for dentists, they told him.

He said however that his workday ended about 5 or 6pm. He also knew that in many jewelry shops the boss stayed late and that is when he would call on jewelers. This was much better than loafing around in a hotel.

A few years later he was again summoned into the executive offices. He was told that the orders from his

territory had been examined and orders from jewelers far exceeded those from dentists. And they would like to promote him to be a vice president.

Basically investment materials are still about the same as they were then, however changes to better fit jewelers needs have been made over the years. The Kerr Corporation (reference 7) says that the main ingredients are 70 to 75% silica (SiO_2) in two forms, quartz and cristobalite. The other large ingredient is 25 to 30% plaster of paris ($CaSO_4 \cdot \frac{1}{2} H_2O$). Some materials in the amount of about 1% are added to help control setting behavior, fluidity, wetting and vacuum rise. I have been told also strength.

In this paper and in the following Chart #1 this 1% is ignored. We also assume a silica content of 75% and a plaster of paris content of 25%. We also assume a water addition of 40% as is commonly specified.

When water is added part of it is collected by the plaster of paris to form crystals of gypsum ($CaSO_4 \cdot 2H_2O$). The solidified gypsum thus creates a fairly strong mold. The considerable excess water fills voids between investment particles and provides the fluidity needed to accurately surround wax models.

Cris Cart (reference 6) says that water temperature is important, cold slows and warm speeds setting. Successful casters often use special care for investment powder storage conditions and water temperature and quality.

Although there is much excess water the amount is important. Schneller (reference 1) says that added water

increases porosity. I expect that this also affects surface quality and strength.

Kerr says (reference 7) that during burn out the gypsum loses its water the cristobalite goes through a phase change that involves expansion. This compensates for shrinkage of the gypsum. This results in some compression that helps hold the system together.

When I look into Langes Handbook of Chemistry (reference 2) I see the calcium sulfate has some solubility that amounts to about 0.1 gram per 100 grams of investment. This is not much but could act as a bond at contact points of investment particles after dehydration is complete.

In the following Chart #1 we try to show what happens when a mold flask is heated. This is based on chemical data given in Lange (2) for investment materials at laboratory conditions.

In the real world of jewelry casting we can expect these changes to go much as in the lab conditions, however, the slow heating of a flask means that changes at the surface go first and proceed inward with time.

At a temperature of about 55°C (132°F) wax begins to melt. As temperature rises to 100°C (212°F) water boils away although some drying occurs earlier. Then at 127°C (260°F) the gypsum begins to lose water and revert to plaster of paris. At 160°C (325°F) more water departs and plain anhydrite ($CaSO_4$) is formed.

It has been recommended that flasks should be very wet when this "burnout" is started so that the water and

water vapors created will help drive the wax out of the investment. The practice of steam dewaxing may reduce the amount of wax that soaks into the investment. It does not prevent it.

In Chart #1 the quantities involved are shown to scale vertically. Heating time creates certain changes and is shown horizontally but not to scale. The plaster of paris is assumed to be 25%. Water added is 40%. Small other additives are ignored although they may provide important qualities.

As temperatures increase any residual wax is carbonized. This is at about 350°C (660°F) by my tests. Carbon is known to cause defects and must be removed.

Carbon is a solid at all reasonable temperatures and pressures. Only at about 1000°F (540°C) does it become active enough to react and be removed in a reasonable time. This was our experience with all the various carbon removing materials we tested.

The convenient way to remove carbon is to heat the flask to about 1250°F (675°C) and allow air to burn it to CO or CO_2. The airflow through flasks is usually slow so this temperature is maintained for several hours.

According to Lange (1) 100 ml of water will dissolve about .100 grams of gypsum. In my opinion this dissolved portion may be a binder to cement investment particles together. Other materials may be added to further increase strength. My tests show that boric acid additions make a stronger mold.
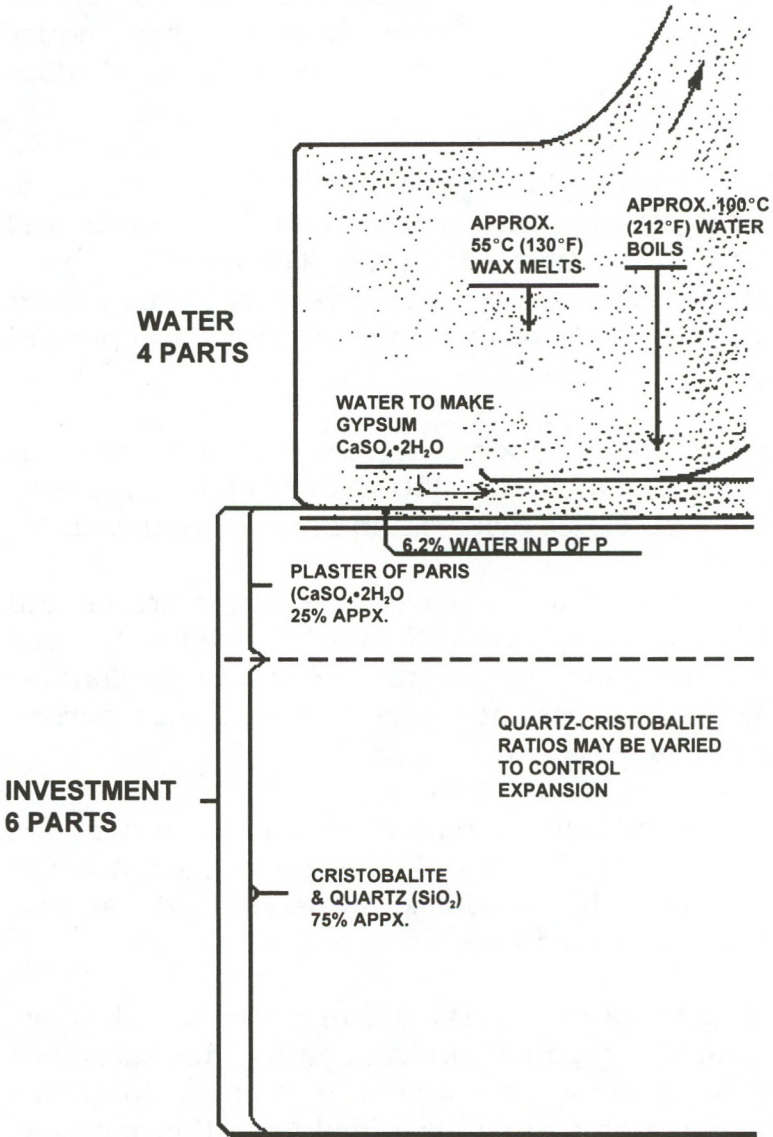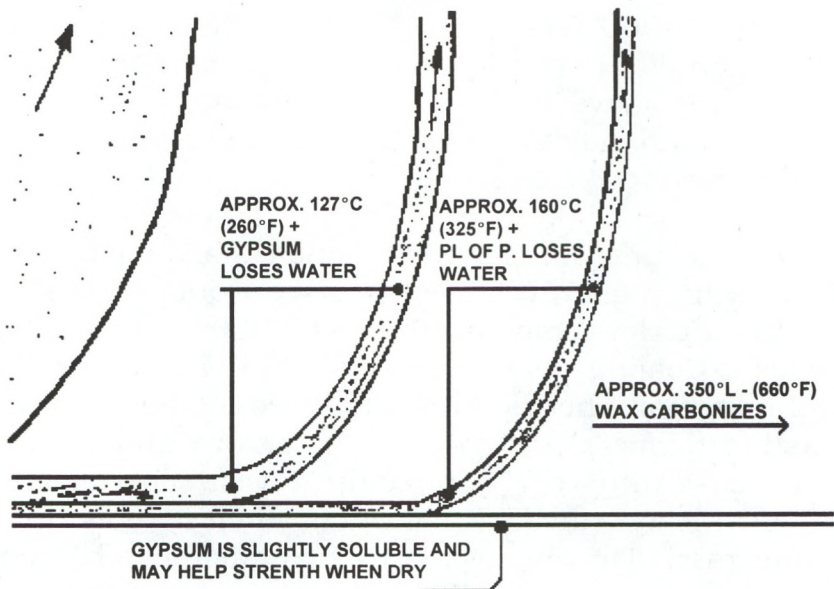
WATER 4 PARTS

APPROX. 55°C (130°F) WAX MELTS

APPROX. 100°C (212°F) WATER BOILS

WATER TO MAKE GYPSUM $CaSO_4 \cdot 2H_2O$

6.2% WATER IN P OF P

PLASTER OF PARIS ($CaSO_4 \cdot 2H_2O$ 25% APPX.

INVESTMENT 6 PARTS

QUARTZ-CRISTOBALITE RATIOS MAY BE VARIED TO CONTROL EXPANSION

CRISTOBALITE & QUARTZ (SiO_2) 75% APPX.

CHART #1

APPROX. 127°C
(260°F) +
GYPSUM
LOSES WATER

APPROX. 160°C
(325°F) +
PL OF P. LOSES
WATER

APPROX. 350°L - (660°F)
WAX CARBONIZES

GYPSUM IS SLIGHTLY SOLUBLE AND
MAY HELP STRENTH WHEN DRY

BURNED OUT INVESTMENT
LOSES ABOUT 80% OF
ITS STRENGTH AND IS ABOUT
HALF AIR

LAB TESTS SHOW USE OF
BORIC ACID AS 20 GRAMS PER
LITER OF WATER MATERIALLY
INCREASES STRENGTH

INVESTMENT MIXING & HEATING

The traditional way to cast has been to cool the flask to about 800-900°F (425-480°C) at which time the molten metal is poured. I am told that casting is now often done at temperatures above 1000°F. It is likely that many castings are poured into molds much hotter than is realized because the investment cools so slowly.

At one time I removed a 4 inch diameter by 6 inch high flask from a 1250°F oven and set it out in the shop at 72°F, the interior temperature reached 800°F only after 32 minutes. Cooling such a flask to 800° in an 800° oven would take many hours. Shops that reduce burn out ovens to casting temperature for an hour or two and then pour usually cast into very hot molds. Investment expands a little when it is heated. It contracts when it cools but at a different rate. The engineer calls this difference hysteresis. In my early casting work Kerr provided a hysteresis curve for their satin cast. When heated and then cooled the original dimensions were reached at about 800-850°F (425-460°C).

I feel sure that casting at this temperature and the use of an asbestos paper lining in the flask was the need for dentists to get very accurate dimensional reproduction.

I found this to be very important when I tried to make some large paper thin gold castings for DuPont. Only when I used care to get the mold to 800°F could I get a complete casting.

I have seen hysteresis curves of some Kerr investments now being made for jewelers. They are quite different from that of many years ago. It is likely that this investment is specifically designed for jewelers where small dimensional changes are not important.

Early in this century the high temperature chemistry of some materials of interest in ore processing work was explored. This was done by Hofman & Mistowitsch at the Massachusetts Institute of Technology. I refer to these as references (3) and (4). The high temperature reactions of calcium sulfate ($CaSO_4$) alone, when mixed with quartz (SiO_2) and with carbon (C) were carefully measured.

Calcium sulfate, quartz and carbon are the materials of investment and wax so we were hopeful that this long ago work could be used in a study of investment.

Information reported in references (3) and (4) as well as some data that we developed are given in Chart #2. Section A shows some temperatures involved in the thermal decomposition of Calcium Sulfate ($CaSO_4$) as reported in (3) and (4).

When quartz (SiO_2) is added a chemical reaction starts at a lower temperature. See Section B of Chart #2. This produces Calcium Silicate and Sulfur dioxide - ($CaSO_4$ + $SiO_2 \rightarrow CaSiO_4$ + SO_2). They were careful to test different ratios of calcium sulfate and quartz and found that all reacted in the same temperature range, only producing different amounts of products. This led us to believe that investment would react similarly at such temperatures even though investment mix ratios are different.

When carbon is present new reactions begin at even lower temperatures. These are well within the melting range of jewelry alloys. The results reported in reference (4) are shown as C in Chart #2. These reactions produce gases such as CO, CO_2 & SO_2. Also produced is Calcium Sulfide (CaS) reported to be a notorious sulfurizer.

CHART #2   **HIGH TEMPERATURE CHEMISTRY OF CALCIUM
SULFATE, QUARTZ & CARBON
A B & C - HOFMAN & MOSOWITSCH
REFERENCES (3) & (4) 1908-1910
B_L, C_L & C_N - LOEWEN, 1998**

B   REACTION $CaSO_4$ + QUARTZ MIX
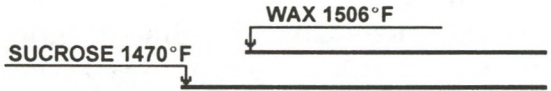$CaSO_4 + SiO_2 \rightarrow CaSiO_4 + SO_2$

B_L   3 SAMPLES INVESTMENT TESTED MAY 98

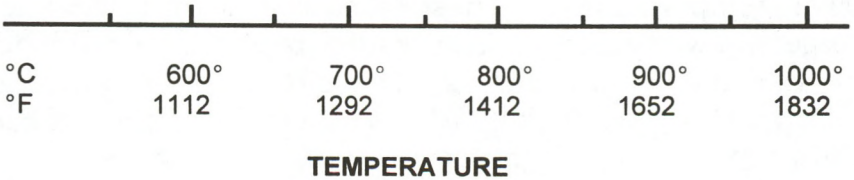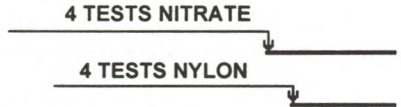**C**   WITH SUCROSE DERIVED CARBON LOWER
TEMPERATURE REACTIONS OCCUR -
  1. REACTIONS START - 1300°F
  2. MOSTLY $CaSO_4 + 2C \rightarrow CaS + 2 CO_2$ - 1470°F

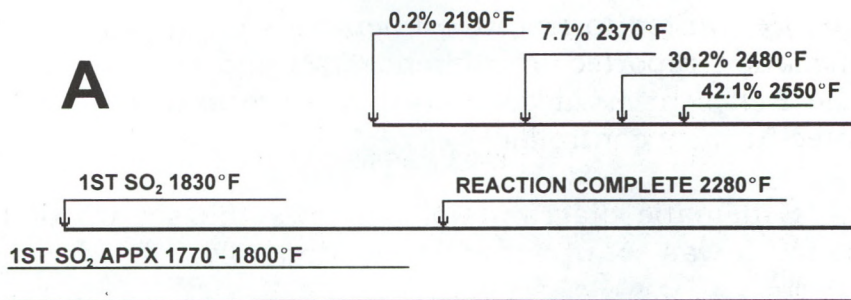| 1	2	3	4
↓	↓	↓	↓

C_L   WAX 1506°F

SUCROSE 1470°F

INVESTMENT WITH
CARBON -SO_2 EVOLVED
TESTED MAY 98

C_N   4 TESTS NITRATE

4 TESTS NYLON

°C	600°	700°	800°	900°	1000°
°F	1112	1292	1412	1652	1832

TEMPERATURE

A

0.2% 2190°F — 7.7% 2370°F

30.2% 2480°F

42.1% 2550°F

1ST SO$_2$ 1830°F   REACTION COMPLETE 2280°F

1ST SO$_2$ APPX 1770 - 1800°F

3. $3CaSO_4 + CaS \rightarrow 4 CaO + 4 SO_2$ - ENERGETIC 1560°F
4. MOSTLY $CaSO_4 + 4C \rightarrow CaS + 4CO$ -1650°F
5. REACTIONS ESSENTIALLY COMPLETE - 1830°F

5
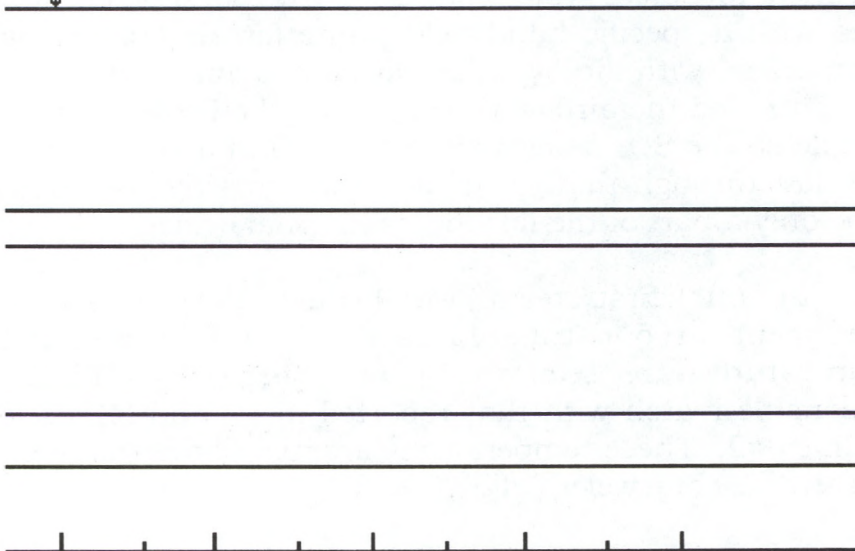
| 1000° | 1100° | 1200° | 1300° | 1400° | °C |
| 1832 | 2012 | 2192 | 2372 | 2552 | °F |

TEMPERATURE

We wanted to test investment to see if it would fit the information reported in references (3) and (4). To do this Eddie Bell sent us a good tube furnace and an excellent Neutec furnace controller.

Schematic diagram No. 3 shows the set up of this system. It was set up for SO_2 detection only.

The work done at M.I.T. and reported in references (3) and (4) was done with careful collection and measurement of materials and reactions were carefully determined. Our tests were set up only to detect the temperatures at which SO_2 evolution started. We did not measure quantity.

We used Draeger SO_2 detection tubes. These were designed to detect from 1 to 25 parts per million, when used with a specific hand held pump for air quality tests. Comparison with airflow in our system is only approximate. We controlled the airflow through the tube furnace over the sample so the SO_2 detector was reached in about 1 second. The flow through the SO_2 detector was positive but limited to be only a part of the flow by its internal orifice.

In our first tests we heated three brands of investment in our tube furnace. The SO_2 production temperatures are seen in B_L in Chart #2. This is a reasonable match with that reported in (3) and (4) - See B in Chart #2. These temperatures are just above the melting temperature of jewelers alloy.

We then mixed wax with investment in one sample. We also created carbon by mixing sucrose (table sugar) in another sample of investment. These were run in the tube furnace and SO_2 was detected from both samples at about
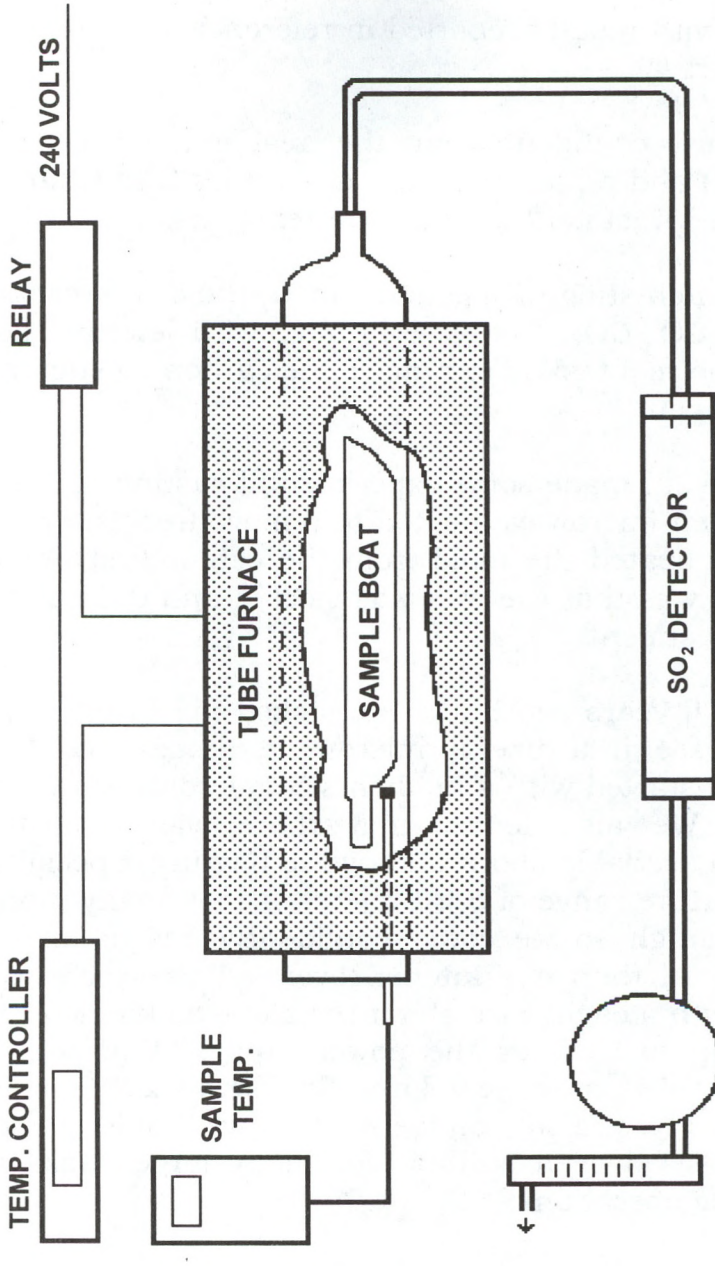
DIAGRAM #3 - TUBE FURNACE SYSTEM

the same temperature (see C_L in Chart #2). Also note the agreement with results reported in reference (4) and shown as C in Chart #2.

We are confident that the reactions reported in reference (4) and reported as 2, 3 & 4 under C in Chart #2, also explain investment plus carbon reactions.

It is interesting to speculate about the exact reactions things like CO, CO_2, CaS & SO_2 have with jewelry alloys. However, the real task is to remove the carbon so such evils can not happen.

In 1992, I made some experimental castings in molds that had been microwave heated to remove free water. The microwaves heated the mold from the center first and my observation was that the wax was ejected and did not soak into the investment.

Several years ago Eddie Bell asked me to investigate further to see if a useful microwave process could be devised. We started with a kitchen size microwave and total ignorance. We also found that there was almost no information available about microwave heating especially in the temperature range of our project. It took many months to learn enough so we could confidently design an oven more powerful than our kitchen oven. This second oven was built with a cavity size about the same as kitchen units but with up to 6 times the power input. With this we learned that we could heat large flasks to 1200°F in one hour. We were also confident that we could build a production sized oven suitable for many large flasks and large casting operations.

We also learned that it would be very expensive and that a prudent engineer would as a next step set up an intermediate size to test things not yet well known. This would be a very costly project even if the industrial size magnetrons were only leased for the project. So this work was shelved.

During this microwave work Eddie Bell and I discussed a lot of ideas. I listed some possible carbon removers and most of them we eliminated as obviously unsuitable. A few mixes were made and most did evil things to the investment. Our goal was to find an additive that would restored the investment to near its non-carbon stability. So we reviewed our previous lists and tests and added a few. We reviewed some of our previous work as a scrap gold refiner and looked at the chemical and physical properties listed in handbooks. Again most of these materials were not usable.

A few were mixed with investment paying careful attention to viscosity, set time, etc. One or two materials seemed useful and further work was done with them by heating them in the tube furnace.

We made 30 or 40 tube furnace tests each taking about 1 or 2 hours but with a long cooling time so the rate was only about 1 per day. We will not clutter this report with materials that did not work.

All these tests were done with investment that had been mixed with water containing sugar so the dry mold would contain 0.5% carbon.

The most effective material in our first series of tests was calcium nitrate $(Ca(NO_3)_2 \cdot XH_2O)$. This is very soluble

so it is conveniently dissolved in the mix water. We found it best to increase the amount of water used for the mix to compensate for the fact that it was no longer 100% water. Other than that no change was needed to make a good mold.

We tested samples with various amounts of calcium nitrate in the mold and found that as little as 4% resulted in an SO_2 emission temperature of about 1750°F (950°C), essentially the same as investment with no carbon, see B_L on Chart #2.

We then started to make regular gold and silver castings and these tests indicated that a 5% calcium nitrate content was best. We made castings in molds that had been briefly heated to 1250°F (1075°C). At this temperature the dark carbon color disappeared in just a few minutes, an important reduction in burn out time.

We found that the flask would not devest by plunging into water but had to be mechanically opened. The calcium nitrate was acting as a cement, binding the investment particles together.

When gems are cast in place, boric acid is often used as a protective material. We understand that this also makes a mold that is reluctant to devest and must be mechanically removed form the flask.

We made up a sample with sucrose and also 20 grams of boric acid per liter of mix water. The boric acid speeds up set time (gloss loss) a little but a very small addition of citric acid nicely corrects this.

The difficulty in devesting the boric acid and calcium nitrate samples renewed our interest in the strength of molds. We set up a simple way to test the strength of molds but our feeling was that these room temperature tests probably gave little information about strength at casting temperatures where it is important.

We modified our methods so that the sample could be tested inside an oven at selected temperatures. We used a length of 1 inch x 1 inch aluminum angle to cast a triangular sample. For our tests we made mixes of a regular water mix, one with boric acid and one with calcium nitrate. We made 2 samples of each mix.

All samples were heated to 1200°F (650°C) and then tested by measuring the breaking strength as shown in Sketch #4. The sample was set up on Vee saddles on firebrick stands as shown and the door closed. When the temperature re-stabilized for a time at 1250°F a steel rod was carefully inserted through the oven top and the empty bottle set on top. A jet of water was opened to start filling the bottle. When the sample broke the bottle dropped below the jet so we had an accurate breaking amount that we could weigh.

The oven was then lowered to 900°F (480°C) and stabilized and the tests repeated.

We believe that if samples are prepared and set up in the same way this fairly simple method could be useful in evaluating investment additives. We made no further tests but our later experience gives confidence that a mold that is both stronger and more open or porous could be designed.

WATER JET

SAMPLE SECTION

1"   1"

SAMPLE

4"
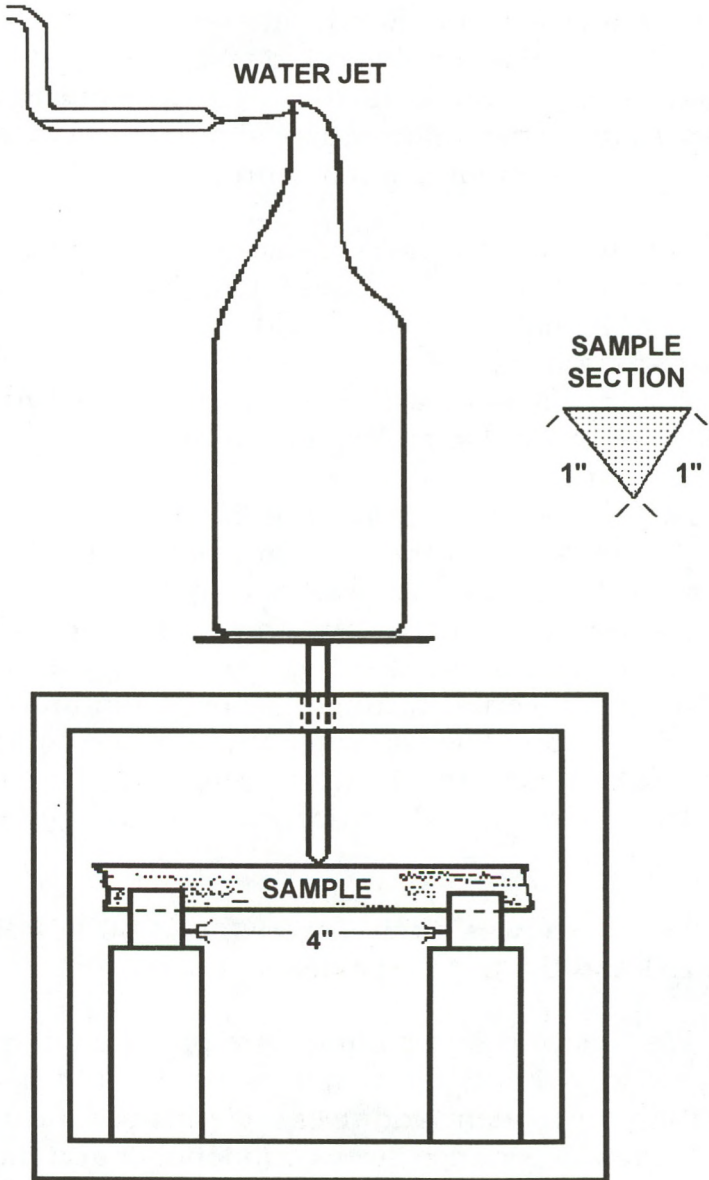
VIEW INTO BURN OUT OVEN
SKETCH #4

These hot tests showed that calcium nitrate gave more strength at 900° than at 1200°F. This was an expected result. The melting temperature of calcium nitrate is listed by Lange (2) to be about 1050°F and would be a liquid at 1200°F but at 900°F be a solid and thus a better cement.

Boric acid according to College Chemistry (5) goes through several changes. At 212°F it loses water -

$H_3BO_3 \rightarrow HBO_2 + H_2O$
then at 280-320°F another water loss occurs
$4HBO_2 \rightarrow H_2B_4O_7 + H_2O$
at higher temperatures
$H_2B_4O_7 \rightarrow 2B_2O_3 + H_2O$

At a temperature of 1200°F the B_2O_3 is above its melting temperature listed by Lange (2) as (577°C) 1070°F), but this is a glass and glasses are known to be viscous materials and the B_2O_3 glass probably acts as a cementing agent. Here again strength at 900°F was higher than at 1200°F. Boric acid was a better strengthener than calcium nitrate.

These very few tests are useful indicators but a series of duplicate tests should be made before really reliable numerical comparisons can be made.

A strengthening cement we felt could reduce porosity and interfere with air flow through the mold. Using some equipment in our shop we set up a method to measure airflow through various samples. This assembly is shown in sketch No. 5.

SAMPLE

FLOW METER

MANOMETER

PUMP

VALVE
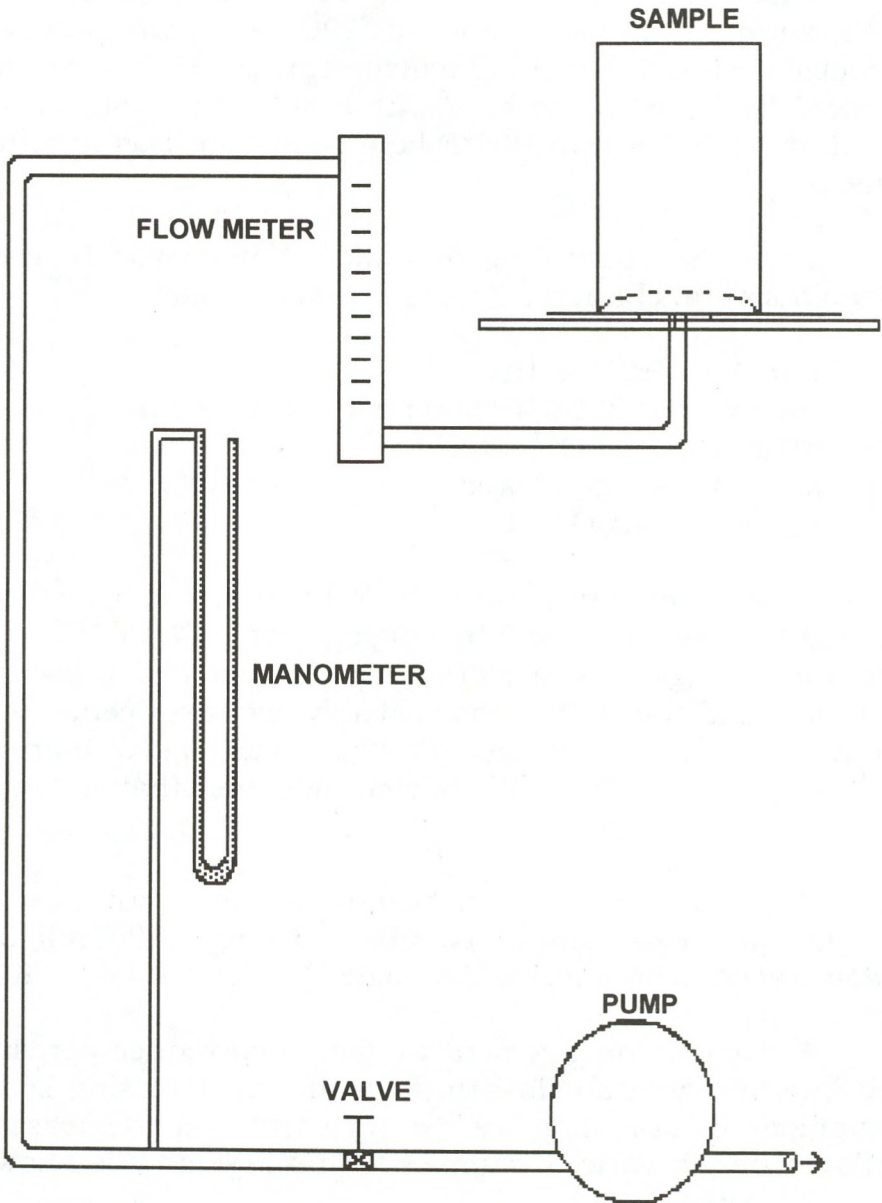
**FLOW TESTING
SKETCH #5**

For our few tests we used 2 inch diameter by 2½ inch high flasks. The bottom end was carefully ground smooth for a good seal. A viscous oil was used between the gasket and the flask during the test. The vacuum applied was controlled with a valve and measured with a manometer.

We found no significant differences in our samples. There may indeed have been porosity differences. We think longer samples should be tested.

Several years ago Eddie Bell tested various organic particles to see if a more open porous mold could be made. Samples were prepared with wax models in the flasks but they were heated bottom up so the melted wax could not run out. Samples containing small particles of nylon fiber and cellulose when heated to burn out temperatures became completely white (carbon free).

These and other materials were sent to me and rather unscientifically tested between phases of other work.

Our first tests were very rough and ready. Material identity was iffy and confusing and after a time we lost interest.

When we got the tube furnace and the good Neutec controller we tested rayon (a cellulose derivative) and nylon flocks. We found these and other cellulosic materials were effective in removing carbon. This was determined by the fact that the dark carbon stain disappeared from the molds and we used the tube furnace to measure the temperature at which a sample containing such flock started to emit SO_2. C_N in Chart #2 typically shows these materials do remove carbon.

This is to us and to the nylon chemists at DuPont very surprising. In our search for an explanation we found a possible reaction in college chemistry (6) p. 657). In a volume on coal technology (8) p. 118, 119 and 348) the use of tetralin a hydrogenated double ring compound is described as useful in liquefying coal. The temperature needed is similar to carbon burn out.

Both nylon and cellulose are ring or ring derived structures. Both contain a lot of hydrogen and could possibly hydrogenate the carbon to a volatile material. Very speculative but the only idea we have.

At the time of this writing small jewelry casting tests are in progress near Houston and also by Tony Eccles at a larger scale at APECS, in Victoria Australia. Not enough work has been done to be sure, however, the nylon flock even as fractional percent additions seems to degrade surface smoothness. With nylon there is an odor during burn out. For these reasons, we do not at this time believe that nylon or other flock is of interest to jewelers.

Calcium Nitrate is a good carbon remover and mold strengthener. It is easily and quickly added as a mix water solution, it is not costly.

It does not devest by a simple water quench. A strong water jet or similar action is needed to remove castings.

We have found that all of our carbon removing reactions go best at about 1000-1200°F. This is true whether removal is by air oxidation calcium nitrate reaction or nylon.

We have also found in a few quite preliminary tests that if a flask is heated to say a 900°F casting temperature it will still contain carbon.

If at this time the molten metal is poured its high temperature ignites the calcium nitrate carbon removing reaction at the metal to mold interface. As this is written not enough castings have been made to know if the gases that are created are harmful to castings.

If such a program would consistently give good castings, a considerable reduction in heating costs and heating time may be possible.

References

(1)   Dave Schneller, Lafayette, CO, Verbal Communication.

(2)   Langes Handbook of Chemistry, 10th Edition.

(3)   Transactions of the American Institute of Mining
       Engineers, Vol. XXXIX, 1909.

(4)   Transactions of the American Institute of Mining
       Engineers, Vol. X4, 1911.

(5)   College Chemistry, Nebergall, Schmidt and Holzclan,
       5th Edition.

(6)   Advances In Investment Casting Materials,
       Christopher J.Cart
       Gold Technology, pp. 18-20, April 1998.

(7)   Platinum Casting Investments by Grierson and
       Spaasky,
       Platinum Manufacturing Process Vol. IV, Page 21.

(8)   An Introduction to Coal Technology,
       2nd Ed., Norbert Berkowitz.