THE DEVELOPMENT OF A SELF-DISINTEGRATING CORE-BODY FOR USE IN AN ART BRONZE-CASTING FOUNDRY WHICH EMPLOYS THE CERAMIC-SHELL INVESTMENT TECHNIQUE

by

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Table of contents

Abstract

The development of a disintegrating core-body for use in an art bronze foundry, which employs the ceramic shell investment process, begins with an investigation of four principal materials that will constitute the core formula.

The specifications for the disintegration of the designed core-body formula fall within the parameters that are normally set and used in the ceramic shell art bronze casting process.

The *raison d’ être* for the disintegrating formula is based on the premise that cement breaks down (spalling) after being subjected to heat above a certain temperature. It was shown that pure cement in the form of naked test bars 100 mm x 20 mm x 20 mm does indeed break down into separate pieces when fired to and above 900^0C; where 900^0C is the lowest recommended temperature required for sintering the ceramic shell investment mould.

The addition of calcium carbonate to pure cement in the form of naked test bars, produced a more unified formula that did not break into separate pieces when fired to 945^0C. However this combination of cement and calcium carbonate had a slow setting time of 12 hours and a shrinkage value of 2,3%, which were both above the parameters being sought for a quick-setting formula with a shrinkage value of below 1%.

The combination of cement, plaster of paris and silica produced formulae that set within six hours and had shrinkage values of less than 1% but did not disintegrate within 72 hours. It was only after the addition of calcium carbonate to the these mixes that formulae resulted that set within six hours, had relatively low shrinkage values and showed signs of breaking up after 60 hours.

It was further shown that by altering the ratios of cement, plaster of paris, calcium carbonate and silica, that the parameters for quick-setting formulae with shrinkage values of 1% and below, that also disintegrated within 55 hours, could be achieved.

It was also proved by subjecting these formulae to higher relative humidity conditions that the disintegrating times could be reduced and brought to below 48 hours.

Selected formulae were then subjected to temperatures of between 900^0C and 1000^0C. It was found that as the temperatures were increased so the disintegration times were reduced and were even further reduced under higher relative humidity conditions.

It was found from the above experiments that the selected formula determined to be suitable in all respects as a disintegrating core-body was too difficult to remove from the hollow bronze cast when subjected to an actual bronze pour. Further experimentation using increased proportions of silica in the formula resulted in a final core-body that could be quickly and easily removed from its bronze cast as soon as the core-body had cooled to room temperature.

The selected core-body formula (F21D) that was used in the final set of bronze casting procedures was found to function optimally when fired to a temperature of 900^0C and could be quickly and easily removed from the bronze casts leaving a clean inner bronze surface, free from any remnants of the fired core.

The document concludes by recording the delimitations and advantages of the final core-body formula F21D, as well as making recommendations based on these parameters for further study relating to disintegrating core-body formulations.

CHAPTER 1

INTRODUCTION

1.1 Background to the problem

1.1.1 Brief history of the foundry at the PET.

The Port Elizabeth Technikon (PET) sculpture department provided bronze casting as a study option using the luto method (cf. glossary) for many years. The luto method is an ideal process for small art bronzes as it is has been well proven all over the world.

Phillips Kolbe, the resident sculptor and senior lecturer at the PET, began experimenting with the ceramic shell process as early as 1984. The experiments he conducted were primarily a tentative experiment concerning the possible use of the ceramic shell investment method as an eventual replacement for the luto method at the PET foundry. Nicholas Allen, co-lecturer in sculpture from 1984, also utilized the luto method.

Phillips Kolbe retired in 1990 and David Jones succeeded Nicholas Allen as the lecturer-in-charge of the Sculpture Section in 1992. He immediately abandoned the luto method in favour of the ceramic shell method for all the studio bronze castings from that point on. David Jones also conducted many experiments over the years regarding the formulation and the application of the ceramic shell to wax moulds.

The sizes of the hollow sculptures produced and cast at the PET studio foundry are generally smaller art pieces with larger pieces reaching up into the region of thirty centimeters tall with volumes averaging around one and a half to two litres. Typical hollow art pieces that are sculptured at the PET, including the larger hollow figure study or the hollow mask wax models, are illustrated in the photographs below. It is within these size parameters that a disintegrating core formula will be specifically developed in this study.

Figure 1.1 A photograph of a hollow wax torso (with a volume of approximately one and a half litres. The hollow art piece on the right, illustrates a typical mask sculpture which is built around a hollow tube approximately 300 mm x 30 mm with a volume of 200 ml.

Generally, hollow bronzes that are larger than one and a half litres in size are made by cutting the wax model into sections which does away with the problem of having a core. These sections are then individually invested in the ceramic shell mould. After casting in bronze the sections are cleaned and welded together restoring the models to their original form.

Larger models that specifically require cores, introduce methods and mechanical handling problems due to the combined weight of the core, model wax, steel bracing rods, investment binding wire and the ceramic shell investment that are beyond the scope of the normal small art bronze studio foundry caster and these larger pieces are generally given to industrial art foundries that have the facilities and capabilities to handle larger hollow bronze works. However, the size of the core in this thesis will be extended to the limits of four litres, which gives a general weight of twenty kilograms to be manipulated whilst investing the model in the ceramic shell as well as handling in and out of a hot kiln in the region of 900^0C. This limit of four litres will be to verify that the core that is developed will be functional beyond the vision and scope of the general model size of one and a half litres, normally accepted as the optimum size for hollow cast bronzes in the scenario of the small art bronze casting studio.

1.1.2 Brief overview of the Ceramic Shell Investment method (PET)

In the ceramic shell lost-wax casting method, a thin outer ceramic shell is invested around a wax model, which in the case of a hollow mould will contain a core made from a combination of refractory materials. The completed ceramic shell varies from 5 to 10mm in thickness. The core and the ceramic shell need to withstand the thermal shock of the de-waxing process. The core needs sufficient strength to be suspended within the mould once the wax has evacuated the mould. The core is usually made of materials that harden during the sintering of the ceramic shell investment and it is this sintering or baking process that makes the removal of the hardened core from inside a metal cast so difficult to remove. Various ingenious methods of extracting the core from the cast model have been devised, which include mechanical and chemical methods. These methods require specialist equipment as well as skilled operators to perform.

1.1.3 Problems with Sacrificial Cores

Although the ceramic shell investment method has been improved over the years at the PET and now gives excellent results, the extraction of the core from hollow castings has remained a problem in that the core has to be mechanically removed. This is a difficult and time-consuming process and it can take many hours to complete in removing the last remnants of the core. Experiments have been conducted to try and alleviate this problem, but have met with only limited success.

The fundamental problem with using sacrificial cores (cf. glossary) in the context of the ceramic shell investment process, is that all the core formulae (cf. glossary) investigated so far tend to become hard and robust and are difficult to remove, due to the prolonged and high firing temperature necessary to sinter the colloidal silica sol, which acts as the binder in the ceramic shell investment (cf. glossary).

It should be noted that the ceramic shell investment method is used by art bronze foundries in preference to sand castings or the luto method due to the many advantages offered by this method. (A comparative method between the luto and the ceramic shell processes can be read in the book *Methods of modern sculpture* written by Young and Fennel, 1986). Sand castings do not give the fine surface definition required for art bronzes, although significant advances have been made in using the sand casting process for monumental bronzes. The ceramic shell method however requires a higher sintering temperature, between 900^0C to1000^0C (cf. Young and Fennel, 1986:111), as compared to a low 600^0C required for the luto method. In the latter regard, the heating process, apart from melting and vapourizing the microcrystalline wax (cf. def. of terms) contents of the mould, is merely used to drive off any remaining water in the luto mould and core. Incidentally, a temperature of 600^0C is regarded as the lowest temperature required to expel any remaining wax that may have penetrated the luto mould during the de-waxing process. This temperature is arrived at over a forty-hour firing programme.

The firing time needed to sinter a ceramic shell investment, is generally in the region of four hours, depending upon the type and size of the kiln being used. It is well documented that the sintering process is accomplished by the combination of a time-temperature factor and not by temperature alone (Rhodes, 1996: 311). The requisite high temperatures, taken in conjunction with the time required to reach them in the various ceramic shell processes available, precludes many formulae and methods presently being used for core construction and removal. The removal of the sacrificial core from a hollow metal cast has always proved to be a difficult and tedious process and in this regard many ingenious methods have been developed to remove cores from their hollow metal casting. Here, a number of methods have been devised to aid in the removal of the cores from the inside of hollow bronze castings. These various methods are illustrated below, with specific reference to some of the more common practices.

Indeed, one method often employed by the bronze casting industry, attempts to assist the core removal process by cutting complex wax models into simpler pieces so that they can then be cast separately (cf. Young and Fennel, 1986: 34). Here, the separate hollow cast pieces are welded together after the various cores have been removed. Large apertures in the castings can also be incorporated to aid in the removal of the core from the final cast piece (cf. Young and Fennel, 1986: 39). These and similar methods also require tedious repairs, by having to close the apertures through welding or other means.

A second example involves cores which are made from soft refractory materials like kieselguhr (cf. glossary) to try and ease the problem of core removal, but these cores have low structural strength, which can cause the core to break away from its core pins (cf. glossary) within the mould during the pouring process.

A third method currently employed makes use of either hot caustic soda or hydrofluoric acid to leach the core from the hollow cast bronze. Here both the chemicals dissolve the silica core remnants adhering to the inner metal cast. For example, Rolls Royce uses hot caustic soda to remove cores from their aeronautical engine castings (cf. Hurst, 1996: 89). These methods are extremely dangerous and require special rooms, equipment and handling expertise.

All the techniques discussed so far are used more typically in the cores of metal alloy casting involving alloys with relatively high melting points, for example, LG2 or LG4 bronzes (cf. glossary) with an average pouring temperature of 1200^0C. However other solutions are available for metal alloys casting at lower temperatures, for example, sand casting aluminium.

One of these solutions involves the use of graphite, which is bonded to core materials to aid in the removal of the core from castings. The graphite is decomposed to carbon dioxide and carbon monoxide in an oxygen rich atmosphere at between 650^0C to 800^0C being below the temperature that affects the cast metal alloy (cf. source list, US Pat 6428740). The graphite that is burnt off at 650^0C allows the now un-bonded core material to be easily removed from the casting. Unfortunately graphite decomposes well below the relatively high sintering temperatures of the ceramic shell mould process making this process unusable for the ceramic shell process.

Resinous binder compositions, (for example urethanes), have also been used as an aid to core removal. The formulations containing these materials disintegrate at the pouring temperature of aluminium, which is again well below the temperature required for the ceramic shell process. Sometimes this process is aided by the use of shaking-machines and special vibrating tools in an attempt to remove the cores effectively and economically from their metal castings (US Pat 4448907).

Another method involves salt cores, which are discussed in detail in US Pat 4840219 and US Pat 5921312, which can be dissolved from the metal casting using water. Unfortunately, these salt cores degrade at approximately 800^0C (cf. Hamer: 343) and are not suitable for the prolonged high temperature sintering required for the ceramic shell mould process.

Other methods make use of sacrificial cores in castings that can also be electrolytically dissolved as described in US Pat 6221235, but this method is also not suitable for once-off or limited-casting editions made for sculptural pieces due to the high cost involved. The process is particularly suited for preparing shaped articles from metals and alloys such as nickel, cobalt, titanium and the like. For castings made of such alloys, the sacrificial core is preferably made from a material having a high melting point, such as steel. The electro-chemical process involves flooding the core with electrolyte and passing a current through the metal casting to the metal core to be eroded. Unfortunately, bronze will also be affected by the electro-chemical reaction and this will in turn spoil the surface of the bronze.

Finally, a self-destructive core mould for metal alloys is described in US Pat 4043381. The core composed of silicon lanthonide oxinitride or silicon yttrium is heated from 850^0C to 1100^0C for 12 to120 hours, causing the core to oxidize with a large volume expansion and a co-commitment failure of the core material. The broken pieces of core material are then removed from the core. Unfortunately, the upper temperatures involved here would adversely affect the bronze casting.

Ideally speaking, what is required here is a hypothetical process whereby a sacrificial core can be made of materials that will disintegrate within a period of time after the casting process. This process will be invaluable to the small art bronze caster, as it will obviate the tedious process of core removal presently being experienced by foundrymen.

1.1.4 Key characteristics of the core body at the PET

It can be seen that despite the wide range of possible solutions available, such factors do not satisfy the temperature requirements that will be imposed upon the core body, which is a basic requirement to the sintering of the ceramic shell mould. The following characteristics that a core body should possess in the context of the ceramic shell used to make art bronzes are pertinent:

1. Strong and heat resistant to withstand the sudden temperature changes of the de-waxing process at 600^0C (cf. glossary), the sintering process between 900^0C and 1000^0C as well as the mass of the molten bronze during the pouring process at around 1200^0C.

2. Ideally the core should not shrink away from the lost wax mould during the drying stage or during the sintering or casting stages. In reality the core does shrink very slightly, but this is not enough to affect the general art bronze piece being cast, although it would affect the specifications of technically cast pieces.

3. The core should be easily removed from the hollow cast art pieces to lighten the piece for aesthetic reasons and for allowing any welding to take place. Residual core material will interfere with the welding process.

4. The core should theoretically be porous to the gases given off during the casting process. A core vent is usually inserted into the core material to assist with evacuation of gases and steam during burnout. However, it is important that the core is porous (in the case of recipes involving water), to allow water to escape as steam during the de-wax process; otherwise water locked deep inside the core will merely burst the core due to the formation of steam that cannot escape. Reference should be made to salt cores (US Pat 4840219 and 5921312) mentioned before, where the core is not apparently porous yet provides an alloy cast with satisfactory surface finishes.

5. The core should be of such a nature that it could be easily poured in its liquid phase to reach all the recesses within the mould before it sets within the now filled wax form.

This list is not exhaustive, and serves merely to indicate the key positive attributes that a core should possess to be useful to the art bronze caster.

1.1.5 Problems with previous formulae (c.1975-2003)

There are many formulae used in art foundries, each having different idiosyncrasies, and the likes and dislikes of the particular mould maker. It has been found that generally core formulae listed by foundries in literature may vary in quantities and ingredients but they are more or less the same in general character. For example, the core formula used at the PET for many years was as follows:

The core formula:

Crushed refractory brick	1 part
Grog 0,25-0,7mm	2 parts
Plaster of paris	1 part
Silica 0.074 mm	2 part
Sawdust	1 part

(Formula attributed to N. Allen at the PET: 1984 -1990)

This core formula proved to be very successful, especially when used in the luto method (cf. glossary). It also proved to be highly adaptable and Nicholas Allen reports its long-standing success as a base formula for many applications. Indeed, it is possible to add other ingredients to this basic core recipe of two parts silica and one part plaster of paris such as old disused core material, crushed fire bricks, sand, chamotte etc. It even proved to be successful in the ceramic shell investment process although it took a great deal of time to remove it from the hollow bronze cast. The characteristic of this core formula is that it can be fairly easily removed from hollow bronze castings that have been fired to 600^0C over a period of 24 hours which are the normal parameters for the luto mould firing cycle but which still leaves remnants of the core attached in hard to reach areas. Note the firing temperature is only to 600^0C, whereas the ceramic shell process requires a sintering temperature of between 900^0C and 1000^0C.

A second formula used most successfully by the late P. Kolbe also at the PET, had the following formula:

Crushed insulation brick	5 parts
Plaster of paris (Almod 70)	1 part
Glasstone or fibrous plaster	1 part
Sand (clean river sand)	1 part

The Almod 70, a grade of plaster of paris (cf. glossary), produces a harder fired core than does the fibrous gypsum used in the D. Jones formula, however it is structurally stronger and less likely to break away from the core pins during the bronze pour. The downside of using Almod 70 instead of fibrous gypsum is that it is more difficult and time consuming to remove from the hollow cast bronze. This formula comes away fairly easily in parts but in undercuts and difficult to get to areas it is very difficult to dislodge due to its binding properties.

Another core formula presently being used at the PET, by the practising art lecturer, D. Jones, has a slightly different makeup to the formula contributed by Kolbe and modified by Allen.

The general formula (PET):

Luto / old grog / old investment	5 parts
Plaster of paris (fibrous plaster of paris)	1 part
Sand	1 part
Colloidal silica sol	a sufficient quantity to wet the mix

This core formula is structurally successful as a sacrificial core for bronze casting, but still exhibits the property of being difficult to remove from the hollow-cast bronze. The colloidal silica acts as a binder in addition to the fibrous gypsum. The one reason for the inclusion of colloidal silica is that it replaces water in the mix and so the core mix can dry in a shorter period of time than if water was used instead. This core is robust and once again as in the P. Kolbe formula above, it is very difficult to remove from difficult to reach areas, which can take a few hours even when using mechanical tools.

The core formulae described above provide qualities suitable for art bronze castings, the one common negative property in them all is that they cannot be easily removed from the hollow bronzes, without reverting to tedious mechanical or chemical means. In consultation with Mr. D. Jones, resident art sculpture lecturer at the PET, it was considered that in the light of the difficulties experienced in removing the PET core material from hollow bronze casts at present, it would be advantageous if a core could be developed that could be easily removed within 48 hours from its bronze cast, with the proviso that it did not have a fired shrinkage greater than 1%. The shrinkage of a core-bodies used in art bronze works, is not of a critical concern when within certain limits, as the thickness of the wax model used for the bronze casts can be adjusted to accommodate the known shrinkage values.

The intention would therefore be to develop a sacrificial core, which completely disintegrates soon after it has served its purpose in the bronze casting process. In this regard such a hypothetical disintegrating core (regardless of its composition) would need to take the following temperature constraints into consideration:

- Firstly, the sudden temperature increases involved in the de-waxing (cf. glossary) process to rapidly expel wax from the mould before the wax can expand and crack the ceramic mould. This process takes place at approximately 600^0C or at red heat.

- The second constraint is that the ceramic shell investment mould requires to be sintered between 900^0C and 1000^0C to produce a robust mould for the bronze pour. This sintering process is usually done in an electric kiln and takes approximately four hours for the kiln to reach the sintering temperature, depending on the particular kiln being used.

- The third constraint is that the molten bronze poured into the mould momentarily raises the temperature of the shell and the core in contact with it at approximately 1200^0C before the cooling process begins.

It is within these temperature constraints that a refractory sacrificial core has to be formulated and still retain the intrinsic characteristic of a good core for bronze casting in the small art bronze foundry;

Other factors besides temperature would also need to be examined prior to the development of a disintegrating core-body. These factors are listed below:

1. The materials that make up the various formulae should be freely available from local suppliers.

2. The process must be simple and should avoid the use of dangerous compounds such as hydrofluoric acid and hot sodium hydroxide.

3. Ideally the removal of the sacrificial core should be as simple as raking or gouging the core from the hollow bronze.

4. The core must be robust to withstand the de-waxing, sintering and the bronze pouring process.

5. The core mix (cf. glossary) must initially be fluid enough to reach all the recesses within hollow wax moulded form.

6. The core must not shrink to such an extent so as to change the inner dimensions of the model being cast, i.e. minimal shrinkage.

7. The core should set within a reasonable time.

8. The core must be refractory to the molten bronze.

9. The core must dry and or cure to a certain degree in the mould after being poured, within a reasonable time, for example seven days which is generally the time taken to invest the wax mould in the ceramic shell mould to achieve maximum strength. (it is a well known fact that a shorter time can be used to invest a wax model in the ceramic shell process, but this can lead to a loss of strength in the ceramic shell mould if each applied layer is not sufficiently dried between each subsequent application (cf. Guerra and Roberts, 1992).

10. The issues concerned with porosity need to be resolved, or the core should be well vented.

11. Firing or sintering temperatures will have to be examined to determine whether the core will be affected at different sintering temperatures.

12. The largest hollow bronze sizes that will be cast with a core, will be in the region of one and a half litres with a height of around thirty centimeters. Larger volume moulds will be made i.e. up to four litres in volume, but these will only be to test the core beyond its designated requirements as stated above. This will be to ensure that if larger hollow bronze casts are made, then a volume of up to four litres will be acceptable for the developed core and still allow it to retain its integrity (cf. introduction to the delimitations).

1.1.6 Supporting research evidence

Preliminary tests have been conducted on the three core formulae discussed in 1.1.5 above. These formulae have been found to be robust and show no signs of disintegrating after having been fired to 960^0C.

Further investigations led to the consideration of using cement as a possible core material. This has previously been used as a mould material as described by Ammen (1980: 400). The cement however is not baked in the formulae described by Ammen when used for bronze casting, yet it withstands the molten temperature of bronze at 1170^0C. In preliminary experimentation, different percentages of cement were added to all of the formulae mentioned in 1.1.5, to test whether this could be a possible aid to the disintegration of the core body.

It is a well-documented fact that cements exhibit a spalling effect (cf. glossary) after it has been subjected to fire. It was for this reason that the experiments using the above mentioned formulae with the addition of various proportions of Portland cement were undertaken. These tests all produced core bodies that became crumbly (to a degree) after being subjected to a temperature of 960^{0}C, but they still required mechanical assistance to remove the core from the cast bronze.

However, there still appears to be a potential factor in the use of cement as an ingredient in a core formula that with further modification and formula adjustments could be used as a contributing agent in the development of a self-disintegrating core formula.

It should be noted that cement on its own does not provide a good substitute for use as a core body, due to its slow setting time as well as the limited effect of the spalling phenomenon, which is more attuned to the breaking up of cement after being subjected to fire due to the inherent moisture content which is bound up in the micro pores within the cement matrix (cf. Connolly, *et al.* 1996: 43).

In the light of the preceding background information it is possible to clearly formulate a research question, viz.:

1.2 THE STATEMENT OF THE RESEARCH PROBLEM

What is the optimum formula for a quick-setting core-body, which is wholly suitable for a wide range of hollow bronze casting activities within the small art foundry context and which will also disintegrate within a specified period of time thus obviating tedious mechanical assistance and/or the use of chemical agents for its removal?

1.3 THE STATEMENT OF THE SUB-PROBLEMS OF THE RESEARCH PROJECT:

1.3.1 Statement of the First Sub-problem:

What materials or combination of materials can be used to produce a quick-setting core formula for use in the ceramic shell process that will disintegrate within 72 hours, under controlled conditions of temperature and relative humidity?

1.3.2 Statement of the Second Sub-problem:

What is the most effective formula that can be developed from the most promising formulae investigated in the first sub-problem, which will ensure that the core-body with quick-setting characteristics will disintegrate within 48 hours after firing and still have a shrinkage value of equal to or less than 1%?

1.3.3 Statement of the Third Sub-problem:

What are the relative humidity considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal studio bronze casting procedures?

1.3.4 Statement of the Fourth Sub-problem:

What are the temperature considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal ceramic shell sintering parameters?

1.3.5 Statement of the fifth sub-problem:

Would the conclusions inferred in the first four sub-problems be applicable to core formula/formulae when used for the actual production of a wide range of hollow bronze casts?

1.4 LITERATURE REVIEW

This literature review will include a general discussion on such pertinent issues as ceramic shell, core moulds, the physical properties of core formulae, the physical properties and use of materials such as plaster of paris, cement, silica, calcium hydroxide and calcium carbonate, water and relative humidity.

More specifically, this review is divided into thirteen definitive topics related to the study of a disintegrating core-body when used in conjunction with the ceramic shell mould. Here, all those authorities who have made a contribution, however limited, to the final formulation of the research methodology are reviewed. In this context, it should be understood, that without the enormous contribution made by these various individuals, this research project could not have been initiated. In this regard, the following issues were examined as regards their possible impact on the proposed investigation, viz.:

1.4.1 The literature review will commence with a short appraisal of the ceramic shell investment processes, including the various attributes and problems associated with it.

1.4.2 Ceramic shell core removal problems will be discussed as these parameters are the very issues that must be addressed in the development of a disintegrating core-body formula.

1.4.3 The desired core properties for a ceramic shell investment will be discussed as these factors will have a direct bearing in the development of a disintegrating core-body.

1.4.4 The issue of carbon removal from the ceramic shell investment will be discussed, which is an essential factor, if the integrity of the outer surface of the bronze mould is to be preserved.

1.4.5 The literature concerning the more traditional core formulations and production techniques will be reviewed as a reference to all necessary properties that must also be represented in the development of a disintegrating core-body.

1.4.6 Issues concerning core permeability and porosity will be examined as these factors are of particular concern in the de-waxing, firing and bronze casting processes.

1.4.7 The issues concerning the employment of cement in core formulations will also be reviewed as cement will form the “backbone” of the research for a suitable ceramic shell core-body with disintegrating characteristics.

1.4.8 Here, binders and quick-setting agents will be discussed in the light of the available literature, with reference to them acting as essential catalysts, so that a quick-setting disintegrating core-body formula can be achieved.

1.4.9 The literature relevant to those issues concerning the usage and roles of aggregates will be reviewed as possible disintegrating aids in basic cement formulations.

1.4.10 Here, chemically active fillers will be discussed as regards their possible impact on a hypothetical disintegrating core body.

1.4.11 The literature relevant to water will be briefly reviewed as regards its employment in any formulae with special reference to plaster of paris.

1.4.12 Relative humidity will be discussed as a possible contributory factor in the desired controlled disintegration of post-fired core formulae.

1.4.13 Temperature considerations for fired core formulations will be discussed within the temperature limits set for sintering the ceramic shell mould when used in the bronze casting process.

1.4.1 The ceramic shell

What follows is a brief review of the ceramic shell process by selected authorities, including Penland (1976), who incidentally was one of the original investigators of the flash de-wax method used for various combustible core materials. The formulation of a self-disintegrating core owes much to the earlier luto method of investment in that certain of the basic ingredients needed for the research have already been tried and tested over many centuries. In this context, Groover (1996: 269) explains luto investment casting as follows:

> In *investment casting*, a pattern made of wax is coated with a refractory material to make the mold, after which the wax is melted away prior to pouring the molten metal. The term investment comes from one of the less familiar definitions of the word invest, which is ‘to cover completely’, this referring to the coating of the refractory material around the wax pattern. It is a precision casting process because it is capable of making castings of high accuracy and intricate detail. The process dates back to ancient Egypt …and is also known as the *lost-wax process*, because the wax pattern is lost from the mold prior to casting.

However, in the case of luto, temperatures are not likely to exceed 650^{0}C and the specific mechanics of a self-disintegrating core body will only come into operation at temperatures produced as a result of employing the ceramic shell investment technique (above 825^{0}C). The ceramic shell technique is therefore the control environment within which all experimentation will reside.

Schnier (Penland, 1976: 20) describes the attributes of the ceramic shell mould as follows:

> Perhaps the greatest advantage of all in the use of ceramic shell molds is the remarkably short time that is required to prepare them for casting. The wax melt-out and burn-out time for these molds may be as short as twenty minutes. This, of course, results in a great saving of time and especially of fuel. It is possible to prepare these molds for casting, i.e., to de-wax and burn out residue while the bronze is being melted in the crucible furnace. And because of their high resistance to thermal shock, small molds can be cast unsupported in sand and shot poured around them for support. Removal of the mold from the casting is simply a matter of a few light blows with a hammer. Where undercuts and depressions occur in the cast it is more difficult to remove the hard ceramic material than it is to remove the softer investment used in solid molds. But by using sharp points the material can eventually be picked out.

It is this latter point that makes what would otherwise be the perfect investment technique (ceramic shell), particularly labour intensive. It is important to note that authors like Mills and Gillespie (1969: 68) make an observation of the difficulties encountered with core removal using the ceramic shell method. This supports the very reason for this research project.

1.4.2 Ceramic shell core removal problems

Mills and Gillespie (1969: 68), explain the procedure of core removal, which they describe as a "tedious process" and go on to state that:

> It is always desirable to produce a light cast. It is absolutely essential if the bronze is to be cleaned with acid. The acid will soak into the core and give rise to an efflorescence of salts for months afterwards. The procedure is to smash the core with iron rods and wire and rake or rinse the debris out. [Note: the luto core is much weaker after soaking in water.] … If the core is enclosed, overnight soaking may be necessary. Do not soak it for too long, however. The plaster in the core [is] both destroyed and partly restored by baking, and will set again given time.

As is well known, where the ceramic investment is used as the core material, even greater problems arise for core removal, due to the inherent characteristics of the sintered ceramic material. However, the core materials used in the luto method are more easily removed, but these cores are heated to only 650^{0}C (cf. Mills and Gillespie, 1969: 49), whereas in the ceramic shell mould process, the temperature is in the region of 900^{0}C-1000^{0}C (cf. Young and Fennel, 1986: 111). In addition, Mills and Gillespie highlight a very important point, namely, if one uses water to cool down a ceramic shell investment that has been cored with a more traditional core recipe containing plaster, the likelihood is high that the core will become even more stubborn as far as removal is concerned.

1.4.3 Desired Core properties

As regards, the ideal core property, Ammen (1980: 121), states the following:

> [I]n sand cores when the mold is poured the core holds together long enough for the metal to solidify, then the binder is finely cooked from the heat of the casting until its

> bonding power is lost or burned out. If the core mix is correct for the job, it can be readily removed from the casting interior by simply pouring it out as burnt core sand. This characteristic of a core mix is called its *collapsibility*. The size and pouring temperature of a casting determines how well and how long the core will stay together.

Ammen also states that the ideal core must have sufficient hot strength to be handled and used properly. The hot strength refers to its strength while being heated by the casting operation. Indeed, (during sintering), the core is heated to approximately 900^{0}C to 1000^{0}C, in only a few hours and must still remain robust after being removed from the kiln whilst awaiting the molten bronze.

These (*inter alia*) properties stated by Ammen above, regarding “collapsibility” of the core after the bronze has been poured is the ideal being sought for a core that disintegrates after being fired to between 900^{0}C and 1000^{0}C. Here, Groover (1996: 264), states that “several indicators are used” to ascertain the desired parameters of the mould:

- **Strength:** the mould’s ability to “maintain its shape and resist erosion caused by the flow of molten metal; it depends on grain shape, adhesive qualities of the binder, and other factors.”

- **Permeability**: the capacity of the mould to “allow hot air and gases from the casting operation to pass through the voids in the sand.”

- **Thermal stability**: “the ability of the mold formula at the surface of the mold cavity to resist cracking and buckling upon contact with the molten metal."

- **Collapsibility**: “the ability of the mold to give way and allow the casting to shrink without cracking the casting; it also refers to the ability to remove the sand from the casting during cleaning.”

- **Reusability:** “can the sand from the broken mould be re-used to make other moulds? These measures are sometimes incompatible; for example, a mold with greater strength is less collapsible.”

The feature of permeability (often confused with porosity) is also highlighted by Mills and Gillespie (1969: 34), who go on to describe the normal approach employed when coring a mould but do confirm what most authorities proffer, namely that the more porous the core is, the better the bronze pour will be (cf. Lomax, 2001). Here, the more correct term “permeability” should be used. The core is required to be permeable to a certain degree, to allow any gases evolved during the bronze pour to be dissipated out through the mould via the core; otherwise the evolved gases will be retained in the bronze as it freezes. It must be also noted that the ceramic shell is automatically porous to a certain degree due to the very nature of the sintered colloidal silica, which in turn will allow evolved gases to dissipate through the permeable shell mould. The core also has to be sufficiently permeable to allow water vapour (that has been retained in the core formula) in the form of steam to exit the core during the de-waxing and the subsequent sintering of the ceramic shell mould and the core.

The authors (Mills and Gillespie), note that the curing of the mass of the core is related to the length of the firing time. Here, primarily through the agency of radiation, heat reaches the core last, since it is in the centre of the mould. It is for this reason that a soaking period at the top temperature (to ensure that heat penetrates to the centre of the core) will have to be considered, depending on the volume and mass of the core being heated during the sintering process.

Three temperature considerations will also be taken into account in the experimental procedures when baking the core in the ceramic shell process. These temperatures will be 900^0C at the bottom of the range, an intermediate temperature of 945^0C and an upper temperature of 1000^0C. (cf. 1.4.13 temperature considerations).

The shrinkage values for the core to be developed for art bronze cast pieces is not critical as long as the shrinkage value of the core is equal to of less than 1%. This was confirmed in discussions held with Mr. D. Jones the lecturer in charge for the foundry work at the PET. He explained that as long as the foundry-man knows of this shrinkage value he can calculate it into the thickness of the wax that is used in the lost wax process.

1.4.4 Removal of carbon from luto cores

Theoretically, the total removal of all carbon deposits in a ceramic shell mould should not even be an issue given the high temperatures involved in this particular process. However, if shortcuts are taken by the foundry man, (i.e. inadequate soaking time and/or temperature levels) then resultant wax/carbon residues may be problematic.

Using the luto technique as an example which uses relatively low temperatures, Mills and Gillespie (1969: 47), state that “too much heat will weaken and crack the mould [i.e. a luto mould]”. Mills and Gillespie, who (in the context of luto moulds) warn of temperatures beyond the 550^0C to 650^0C level. This is confirmed by Allen who never took luto moulds much above 600^0C as at this temperature (soaking for about nine hours after a slow temperature rise of some twenty hours or more) one was assured of removing all traces of microcrystalline wax. Mills and Gillespie (1969:47) state that above 750^0C, “a good red heat is fatal” to the luto mould. Mills and Gillespie (1969: 48), also make the following observations:

- The core will “absorb less wax than the exterior, since its moisture is sealed in until the wax melts, but it can still absorb plenty [sufficient wax to spoil the casting].”

- The final strength of the luto mould is in “direct relation to the degree of heat used [absorbed].”

Moisture that remains in the core at the time of the flash de-wax process can therefore be an advantage in preventing the absorption of wax by the core. This consideration will be studied when drying test cores within the hollow wax models. Mills and Gillespie (1969: 47), also state that “The least trace of wax left in the mould instantly generates gases when the molten metal reaches it, causing pitting and holes in the cast, and a small volcano in the runner cup.”

Fortunately, with cores sintered to between 900^{0}C and 1000^{0}C, and for sufficient soaking times (minimum of three hours) the wax is vaporized completely, leaving a clean core and investment mould (as can be visually observed by the pristine white colour of the sintered ceramic moulds) in the normal course of the sintering of the ceramic shell.

Mills and Gillespie (1969: 47) also confirm the obvious, that if a carbonaceous deposit remains in the core, it can ruin the casting:

> This last residue [of carbonaceous material] has to combine with oxygen and burn out. Since there is little oxygen in the kiln after combustion, and any wax residue is embedded in the [luto], a long period must elapse for the oxygen to scavenge it out. It is essential therefore that the mould be 'cooked' at a temperature above 500^{0}C for a considerable time.

This carbon does not appear to be a factor in cores and investment moulds that have been correctly heated to between 900^{0}C and 1000^{0}C.

1.4.5 Traditional core formulae and production techniques

There are a number of authors who discuss core investments in general terms in their books on the subject of bronze casting. For example, Ammen (1980) and Groover (1996) are two authors whose works have been studied and their comments on core investments are noted below.

Ammen (1980: 26) lists various investment ingredients and states that "investment formulae for non-ferrous metals are many, but basically they consist of a binder and a refractory, often combined with various items for increased strength and permeability."

Here, according to him, binders may include:

- Plaster of paris
- Portland cement
- Clay
- Resins

- Silicate of soda

Ammen (1980: 122) also confirms that “a binder should be selected on the basis of the characteristics that are most suitable for the particular use. Some binders require no baking and become firm at room temperature. Examples are rubber cement, Portland cement and sodium silicate or water glass.”

Ammen also sums up the properties that a good binder should posses, namely:

- Strength.
- Collapse rapidly when metal starts to shrink.
- Will not distort the core during baking.
- Maintain strength during storage time.
- Absorb a minimum of moisture when in the mould or in storage.
- Withstand normal handling.
- Disperse properly and evenly throughout the sand mix.
- Should produce a mixture that can be easily formed.

These properties mentioned above by Ammen (1980: 123) will also be applicable to the disintegrating core that will be investigated in this study.

Ammen (1980: 25) further mentions the materials that normally make up the refractory portion of the core formula, namely:

Refractories:

- Silica sand.
- Brick dust.
- Ceramic grog.
- Asbestos.

As has already been mentioned, plaster of paris that is typically used in core formulae (cf. Allen and Kolbe 1.1.5) usually has soft firebrick added to prevent shrinkage, reduce cracking and to increase strength. Talc and crushed firebrick due to their inert characteristics to fire, have no positive contributing properties that can aid in the disintegration of the core after firing and will not be considered in formulating a disintegrating core. Silica sands on the other hand, have the inherent property of thermal expansion and contraction at 573^0C – 575^0C, which could aid in the disintegration of a core, as well as providing strength and the control of shrinkage in a formula, that contains plaster of paris as well as providing porosity to the core.

Thus, plaster of paris will be tried as an ingredient in the investigation for a disintegrating core. As it is already noted that above 750^0C, a plaster of paris mould is destroyed by heat, this factor will have to be taken into account, because the core is sintered to above 1650^0F (900^0C) in the ceramic shell process (cf. Young and Fennel, 1986:111). The specific characteristics of plaster and gypsum will be discussed in 1.4.8 below.

Mills and Gillespie (1969: 35), confirm that the core is more normally manufactured from coarse grog or chamotte and plaster of paris. These ingredients form the bulk of the mould, in the luto process, but here, it is difficult to pour this dampened mix “through a hole less than 1 in. (25 mm.) in diameter.” Here “pourability” will need to be considered for any future core recipes and may well play a vital role in the final formulation.

In addition, the use of cement mixed with suitable sand illustrates the fact that cement and sand are refractory to high temperatures when used for ferrous and non-ferrous metal and alloy castings. This fact combined with the knowledge that cement also exhibits binding and spalling properties is a strong case for its possible inclusion into a core formula with silica sands and perhaps plaster of paris which could produce a compound formula for aiding to the disintegration of a core body after firing to between 900^0C and 1000^0C. Ammen, (1980: 27), discusses cores using bonded sands and then discusses the fact that cement is used in cores for casting. However, the cores in his discussion are not “baked” as is necessary in the ceramic shell process, but the discussion highlights that cement can be used as an ingredient in core formulations. This factor of using cement will be taken into account as a core ingredient for use in a disintegrating core, as cement not only acts as a binder in the pre-fired core but also exhibits spalling characteristics above 900^0C that will be discussed in 1.4.7.4 in greater detail.

1.4.5.1 The effect of the bronze casting temperature on the core-body

The temperature to which the core body is fired will be dependent on the sintering temperature parameters of the ceramic shell investment. Temperatures between 900^0C - 1000^0 C are recommended for the sintering of the ceramic shell when used in the bronze casting scenario (cf. Young and Fennell, 1986:111). However, the temperature of the molten bronze, which reaches at least 1150^0C may have some impact on the core body when the molten metal comes into contact with it during the pouring phase.

1.4.6 Core permeability and porosity

Mills and Gillespie (1969) discuss coring below in general terms and the comments contained therein must be taken cognizance of in all future developments of the disintegrating core.

Mills and Gillespie (1969: 34) go on to describe the normal approach employed when coring a mould but do confirm what most authorities proffer, namely that the more porous the core is, the better the bronze pour will be (cf. Lomax, 2001). The core is required to be porous to a certain degree, to allow any gases evolved during the bronze pour to be dissipated out through the mould via the core; otherwise the evolved gases will be retained in the bronze as it freezes. It must be also noted that the ceramic shell is porous to a certain degree due to the very nature of the sintered colloidal silica, which in turn will allow evolved gases to dissipate through the shell mould. The core also has to be sufficiently porous to allow water vapour (that has been retained in the core formula) in the form of steam to exit the core during the de-waxing and the subsequent sintering of the ceramic shell mould and the core.

The inclusion of additional ingredients in the basic cement formula, for example calcium carbonate, silica or plaster of paris, will aid in making the cement mix porous by default. During the sintering processes of the various testing procedures, the porosity of the core will be observed to have sufficient porosity by default by not exploding or breaking down in any way during the de-waxing and subsequent sintering process as these two processes require the highest porosity values necessary in the bronze casting process.

1.4.7 Cement used as an ingredient in core formulations

Cement is a chemical compound consisting of a number of calcium-silicates and calcium aluminates, which on hydration, releases calcium hydroxide into the mix, which can behave as a contributing factor to spalling of cement that has been subjected to fire. The resultant properties of cement that has been subjected to fire are well documented, but the literature search into the reaction of cement at the specific temperatures between 900^0C and 1000^0C is limited.

The general characteristics of cement however have been reviewed to note as many characteristics of cement as possible that will give an insight into its various properties that will be of value to this investigation.

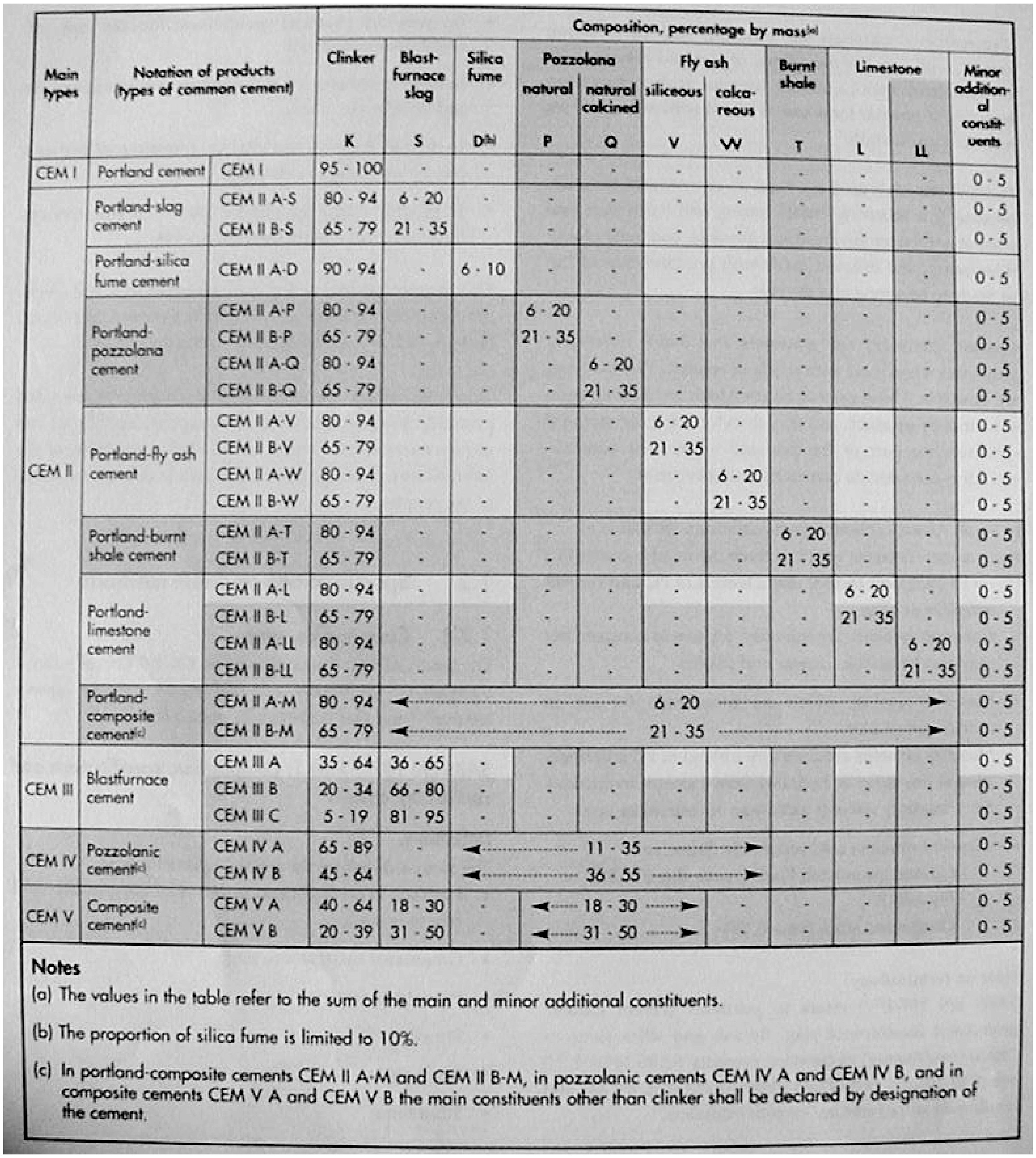
1.4.7.1 Physical and chemical properties of cement

The characteristic of cement is discussed in general below, with an analysis of the actual cement class that will be chosen for this investigation, namely CEM 11 / A-L 32.5 Portland limestone cement. This class of cement is locally produced in Port Elizabeth and also has the property of having added limestone in its formulation, which can be a contributing factor in a disintegrating core formula. Limestone will be discussed under the topic of calcium carbonate in paragraph 1.4.10.1.

The cement type that will be used in this research will be of the type CEM 11/ A-L 32.5 limestone. In consultation with Mr Hermanus Potgieter at the PPC (Pretoria Portland Cement) factory in Port Elizabeth, the following information was supplied:

- After the cement has been heated in the kilns and ground, extenders are added to it.
- A maximum of 6% limestone is added to the cement in the Port Elizabeth factory.
- Gypsum is added to the cement as a set-retarder.
- 32.5 is the strength rating of the cement.

- This cement cannot be simply equated to other cements that are manufactured, for example cements with fly ash added as an extender, as the behaviour and properties are scientifically different in each particular case.



Main types	Notation of products (types of common cement)		Composition, percentage by mass[a]										
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		Minor additional constituents
						natural	natural calcined	siliceous	calcareous				
			K	S	D[b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95 - 100	-	-	-	-	-	-	-	-	-	0 - 5
CEM II	Portland-slag cement	CEM II A-S	80 - 94	6 - 20	-	-	-	-	-	-	-	-	0 - 5
		CEM II B-S	65 - 79	21 - 35	-	-	-	-	-	-	-	-	0 - 5
	Portland-silica fume cement	CEM II A-D	90 - 94	-	6 - 10	-	-	-	-	-	-	-	0 - 5
	Portland-pozzolana cement	CEM II A-P	80 - 94	-	-	6 - 20	-	-	-	-	-	-	0 - 5
		CEM II B-P	65 - 79	-	-	21 - 35	-	-	-	-	-	-	0 - 5
		CEM II A-Q	80 - 94	-	-	-	6 - 20	-	-	-	-	-	0 - 5
		CEM II B-Q	65 - 79	-	-	-	21 - 35	-	-	-	-	-	0 - 5
	Portland-fly ash cement	CEM II A-V	80 - 94	-	-	-	-	6 - 20	-	-	-	-	0 - 5
		CEM II B-V	65 - 79	-	-	-	-	21 - 35	-	-	-	-	0 - 5
		CEM II A-W	80 - 94	-	-	-	-	-	6 - 20	-	-	-	0 - 5
		CEM II B-W	65 - 79	-	-	-	-	-	21 - 35	-	-	-	0 - 5
	Portland-burnt shale cement	CEM II A-T	80 - 94	-	-	-	-	-	-	6 - 20	-	-	0 - 5
		CEM II B-T	65 - 79	-	-	-	-	-	-	21 - 35	-	-	0 - 5
	Portland-limestone cement	CEM II A-L	80 - 94	-	-	-	-	-	-	-	6 - 20	-	0 - 5
		CEM II B-L	65 - 79	-	-	-	-	-	-	-	21 - 35	-	0 - 5
		CEM II A-LL	80 - 94	-	-	-	-	-	-	-	-	6 - 20	0 - 5
		CEM II B-LL	65 - 79	-	-	-	-	-	-	-	-	21 - 35	0 - 5
	Portland-composite cement[c]	CEM II A-M	80 - 94	◄ 6 - 20 ►									0 - 5
		CEM II B-M	65 - 79	◄ 21 - 35 ►									0 - 5
CEM III	Blastfurnace cement	CEM III A	35 - 64	36 - 65	-	-	-	-	-	-	-	-	0 - 5
		CEM III B	20 - 34	66 - 80	-	-	-	-	-	-	-	-	0 - 5
		CEM III C	5 - 19	81 - 95	-	-	-	-	-	-	-	-	0 - 5
CEM IV	Pozzolanic cement[c]	CEM IV A	65 - 89	-	◄ 11 - 35 ►					-	-	-	0 - 5
		CEM IV B	45 - 64	-	◄ 36 - 55 ►					-	-	-	0 - 5
CEM V	Composite cement[c]	CEM V A	40 - 64	18 - 30	-	◄ 18 - 30 ►			-	-	-	-	0 - 5
		CEM V B	20 - 39	31 - 50	-	◄ 31 - 50 ►			-	-	-	-	0 - 5

Notes

(a) The values in the table refer to the sum of the main and minor additional constituents.

(b) The proportion of silica fume is limited to 10%.

(c) In portland-composite cements CEM II A-M and CEM II B-M, in pozzolanic cements CEM IV A and CEM IV B, and in composite cements CEM V A and CEM V B the main constituents other than clinker shall be declared by designation of the cement.

Table 1.1 (cf. Fulton's concrete technology, 2001: 2) Addis illustrates the different types and grades of cement that are available and each one has its own characteristics.

From the table 1.1, it can be seen that Portland cement powder 11 / A-L can have between 6 and 20 parts of limestone. This has been clarified with Mr Hermanus Potgieter (chemist) at PPC (Pretoria Portland Cement) that in fact 6% of limestone is added as an extender at the factory in Port Elizabeth. It can also be seen from the table and in consultation with Mr. Hermanus Potgieter that different other extenders can be added to cement and these additions cannot be simply related one to the other. The development of a disintegrating core in this research will be limited to CEMENT 11/ A-L 32.5 Portland limestone cement powder and other types of cement powder can be a subject for further research.

Smith (1963: 282), states that cement because of its refractory nature is a fair insulator against heat transmission. The following paragraphs discuss the variables that have a direct influence on this statement as well as indicating areas where further research can be done in seeking a core body with disintegrating properties.

The inclusion of cement powder in a core formula, being a reasonable insulator against the transmission of heat, may be a detrimental factor in not allowing heat to penetrate throughout the core if a soaking period is not allowed for when the top temperature is reached in the sintering of the ceramic mould (cf. 1.4.1).

1.4.7.2 Physical structure of cement pastes

Taylor (1964: 393), states that the “specific volume of cement gel is about 0.567cm^3/g dry weight; the porosity is about 28% of the total volume. Cement gel is permeable to fluids, but its coefficient of permeability is comparatively low, about 10^{-14}cm/sec.” Taylor believes that the principal compound of cement gel is tobermorite gel. “The principal non-colloidal component is crystalline calcium hydroxide. It usually constitutes 20-30% of the weight of dry cement gel, or 1/6-1/5 of the overall volume.”

The lack of permeability of cement paste is demonstrated in that it practically explodes if molten bronze is poured into a pure cement paste mould, apparently due to the conversion of retained water within the mould into steam.

It is this water that is retained within the cement paste that provides the chemical release from cement of 20-30% calcium hydroxide. The calcium hydroxide produced here may aid in the disintegration of a core body containing cement as the calcium hydroxide is converted to calcium oxide at high temperature, which again reconverts slowly over many hours to calcium hydroxide by the absorption of water from the atmosphere.

Powers (1968: 1) confirms that of newly prepared concrete is composed of water, cement and aggregate. He also states that the cement particles acquire their gel coatings during their first few minutes of contact with the water. This gel coat is itself “particulate”, the particles being “colloidal hydrates” of some or all of the chemical constituents of the cement particles.

1.4.7.3 Hydration and strength of cement

The issues of hydration and curing of cement paste are interrelated. Here many authorities provide valuable insight into the properties of properly cured cement paste that will offer a clue to the eventual formulation of a self-disintegrating core.

For example, Lea (1970: 271), reports that for “well-hydrated cement paste, the amount of water retained at 105^0C is in the order of 20 per cent by weight of the anhydrous material, and for a completely hydrated cement paste about 25 per cent.” The hydration of set cement paste is key to the curing process. The calcium silicate content of the cement paste reacts with water to form a gel, which gives cement paste its strength.

In this context, Kellerman states that the period of curing cannot be simply prescribed, and (Fulton’s concrete technology, 2001:216) he confirms that the “curing of concrete should be continued until the curing properties of a particular concrete are developed to the required extent.”

Cognizance will be taken of these parameters as it is intended that a core for use in the ceramic shell process will be enclosed (not totally) in a wax mould for seven days whilst the ceramic shell investment is built up around it. This action will by default retain moisture levels (e.g. impede evaporation) in the freshly set cement.

Grieve (1991: 7.19 paragraph 7.1.5.1) indicates that the specimens tested by him were kept in plastic bags to restrict moisture loss; the moisture conditions were therefore close to saturation.

This method of keeping samples made with cement as an ingredient in test formulae in plastic bags will be imitated by rather making the samples in a silicone rubber mould which will provide a semi-closed environment for the samples keeping them moist for seven days which is closely imitated when core mixes are poured into wax moulds for use in bronze casting processes.

Lea (1970: 177), notes that "all compounds present in Portland cement clinker are anhydrous, but when brought into contact with water, they are all … decomposed, forming hydrated compounds." This action may be represented chemically as follows:

Cement: $3CaO.SiO_2 + H_2O \longrightarrow Ca(OH)_2 + xCaO.ySiO_2.aq.$

In this context, Bogue (1955: 526), showed that $2C_3S + 6H = C_3S_2H_3 + CH$, where C= CaO, S=$SiO_2$, H= H_2O

He also points out that "further evidence bearing upon this matter was cited from published data. Thus, by the equation given above, free CaO, as Ca $(OH)_2$, resulting from the complete hydration of C_3S would be formed in the amount of 24,6 per cent. In the experiments by Bogue and Lerch, 19.2 per cent CaO was obtained at 2 years, indicating that the material was 78% hydrated."

This is extremely important to this investigation because when you hydrate calcium oxide, it converts to calcium hydroxide. In short it expands due to an increase in molar volume and disintegrates. This is exactly the kind of property we are seeking in a disintegrating core body.

Neville (1995: 331) informs us that the average of 87 American cement plants (1991) give a general average of 77% of Portland cement strength after seven days when curing for twenty eight days is taken as 100%. Curing should be under damp conditions to ensure the capillaries within the cement remain open.

Neville (1995: 327), further reports:

> Curing should start at the earliest possible instant and should be continuous. Occasionally, intermittent curing is applied, and it is useful to appreciate its effect. In the case of concrete with a low water/cement ratio, continuous curing at an early age is vital as partial hydration may make the capillaries discontinuous: on renewal of curing, water would not be able to enter the interior of the concrete and no further hydration would result. However, mixes with a high water/cement ratio always retain a large volume of capillaries so that curing can be effectively resumed at any time, but the earlier the better.

The above information has special importance (*inter alia*) to a proposed series of experiments, which strive to make full use of the spalling effect of properly cured cement upon heating. In this context, Ballim and Basson (Fulton's concrete technology, 2001: 142) state that as a general rule, especially when durability is of concern, all concretes should be cured for an equivalent of at least five days of water curing at 22^0C.

1.4.7.4 The spalling phenomenon in cement

Once a cement body has been cured it is susceptible to spalling if subjected to fire. In this regard the following authors make valuable contributions to the debate:

Lea, (1970: 657), noted that:

> Hydrated Portland cement contains a considerable proportion of free calcium hydroxide which loses its water above $400\text{-}450^0$, leaving calcium oxide. If this calcium oxide becomes wetted after cooling, or is exposed to moist air, it re-hydrates to calcium hydroxide accompanied by an expansion in volume which may disrupt a concrete which has withstood a fire without actual disintegration.

This important statement will lead the investigation into adding excessive quantities of calcium carbonate or calcium hydroxide to a cement test core formula to evaluate the effect that calcium carbonate or the hydroxide has on cement which has been subjected to fire and allowed to cool, and then exposed to an atmosphere with a high relative humidity.

Crozier and Sanjayan, (1999: 18), explain that the degradation of concrete, both chemically and physically, under the effects of high temperature exposure can be traced to changes in the phase composition and the microstructure and macrostructure of the concrete as heating progresses. Changes in chemical structure, weakening of the bond between the hardened cement paste and aggregates and dehydration due to free and chemically bound water are some of the processes that lead to micro-cracking and subsequent changes in the porosity and strength of concrete when exposed to high temperature.

Crozier and Sanjayan, (1999: 18), describes the various processes that concrete undergoes as the temperature rises:

> Desorption of evaporable water from the pores occurs up to 105^{0}C. At 120^{0}C to 140^{0}C, the calcium alumino-sulphate hydrates of the hardened paste become dehydrated, destroying the ettringite structure and starting to affect some of the concrete strength. Between 200^{0}C and 300^{0}C, dehydration and compaction of the calcium silicate hydrate phases occur. New structural bonds form in the contact areas between the hardened cement paste and the aggregates. Above 400^{0}C, substantial cracking occurs and irregularly shaped pores develop in the concrete grout. The large $Ca(OH)_2$ crystalline compounds in the concrete facilitate the development of internal stresses resulting in a weakening of the concrete structure. The contact area between the hardened cement paste and the fine and coarse aggregate is also weakened; reducing the microstrength 30%-50%, compared with the values for the temperature range 200^{0}C-300^{0}C.

Crozier and Sanjayan (1999:18), show that above 600^{0}C, the “intensification of microcracks and the dehydration of $Ca(OH)_2$ indicate the starting point for disintegration of a concrete and aggregate structure and eliminate the possibility of reuse after a fire. These significant changes have been confirmed by electron microscope investigations.”

Orchard, (1958: 262), states that the “failure of concrete” under the “action of fire” is as a result of the different expansion rates which occur between the hot and cooler layers of concrete.

He states:

> The opposing actions of the cement which shrinks owing to the loss of moisture to a greater extent, than it expands due to the rise in temperature of the aggregate which expands continuously with a rise in temperature. These phenomena [leads] to cracking and spalling... Flints, siliceous gravels and granites are perhaps the worst aggregates and concrete having these aggregates does not offer high resistance to fire.

Connolly *et al*. (1996: 40), states that spalling is the disintegration of a concrete’s surface on exposure to elevated temperatures. He further states that pore pressure (1996: 43) is one of the contributing factors for spalling to occur. The development of internal pressures within the pores of a heated concrete can lead to what he terms “explosive failure”. His key parameters and measures to reduce the probability of spalling occurring are listed below:

- **Permeability:** “Concretes become more susceptible to spalling at reduced levels of permeability**.** Thus, the probability of spalling may be reduced by avoiding low water/cement ratios, finely ground cements or by including polypropylene fibres.

- **Pore saturation**: “By reducing the amount of free moisture within the concrete through drying, either artificially or through ageing, susceptibility to spalling may be alleviated.”

- **Heating rate**: “The imposed heating rate exerts opposing influences on the development of pore pressure. High rates of heating can generate higher steam pressures but can also lead to cracking.”

Connolly warns that certain types of heat-induced spalling can be extremely dangerous and even explosive. Therefore, if cement is used in future formulae, then cognizance will be taken of the effect of the heating rate that will be imposed upon the formulae during the flash de-wax process at approximately 600^0C and the effect on the formulae. Perhaps the dilution of cement in the core formulae with additional ingredients can avoid this disruptive effect due to pore pressure in cement.

The phenomenon of cracking and spalling produced by the action of cement mixed with siliceous gravels when subjected to fire will be used as a point of departure in the search for a disintegrating core body.

As mentioned before, the ceramic shell investment is sintered to between 900^0C and 1000^0C so this phenomenon of concrete failing due to high temperatures will be used to advantage in future formula experiments.

With the knowledge gained from the above literature, the inclusion of luto, refractory brick as well as chamotte (grog) that were materials chosen by Allen and Kolbe (cf.1.3.3) in a core formula will obviously be avoided in the search for a disintegrating core formula.

1.4.7.5 Colour of fired cement as an indicator

The failure of cement due to excessive heat and its associated changes of colour are closely inter-related in the sense that colour change can be an important indicator of the extent of damage that has taken place to a particular cement body due to exposure to a specific temperature. Orchard (1958: 264) further points out that there is a change of colour in the cement due to heat. He states that “the strength [of the concrete] begins to fall rapidly when a temperature of about 250^0C is exceeded. At 600^0C the concrete may still appear sound but its strength will have been reduced by 60 per cent.”

Neville (1995: 389) reports that concretes composed of siliceous and/or limestone aggregates display a colour change depending on the temperature obtained. He explains as follows:

> As this change is dependent on the presence of certain compounds of iron, there is some difference in the response of different concretes. The change in colour is permanent, so that the maximum temperature during the fire can be estimated *a*

> *posteriori.* The colour sequence is approximately as follows: pink or red between 300 and 600^{0}C, then grey up to about 900^{0}C, and buff above 900^{0}C… Concrete whose colour has changed beyond pink is suspect, and concrete past the grey stage is probably friable and porous.

Crozier and Sanjayan (1999: 18) show that the changes in the macro-structure result in a colour change from concrete to pink. The micro-strength is 70% lower than the initial one, illustrating the weakening of bonds between the hardened cement paste and the coarse aggregates. This is one of the main reasons the strength is reduced under the effects of short-term heating and cooling.

These various authorities indicate that the colour change that occurs in concretes made with siliceous or limestone aggregates should display similar colour changes in formulae made using cement, lime and silica in test core formulae. This could be a valuable indicator in future core formulae tests to determine whether the sintering temperature has occurred long enough to penetrate to the inside of the test cores through radiation.

1.4.7.6 The contribution to shrinkage by cement

In developing a disintegrating core-body with cement as an ingredient, cognizance of all the shrinkage values of the contributing materials will prove invaluable. Here, Neville (1995: 426) writes:

> The change in volume of drying concrete is not equal to the volume of water removed. The loss of free water, which takes place first, causes little or no shrinkage. As drying continues, adsorbed water is removed and the change in the volume of unrestrained hydrated cement paste at that stage is equal approximately to the loss of a water layer one molecule thick from the surface of all gel particles.

Neville (1995: 429) discusses the factors influencing shrinkage. He writes that as far as shrinkage of the hydrated cement paste itself is concerned, shrinkage is larger the higher the water / cement ratio because the latter determines the amount of evaporable water in the cement paste and the rate at which water can move towards the surface of the specimen.

These shrinkage facts will be taken cognizance of when conducting tests and shrinkage values taken from the time the core material is poured into test moulds to the time it has been fired to within 900^{0}C and 1000^{0}C will need to be investigated. The heat liberated by the molten metal during the bronze pour and during the cooling phase influences the investment mould as well as the core. The core has to be sufficiently strong and refractory at this temperature of approximately 1200^{0}C, which is at least 200^{0}C above the sintering temperature of the ceramic shell mould and core (cf. 900^{0}C to 1000^{0}C). This effect of the bronze temperature on the core will be taken cognizance of in future core experiments.

1.4.7.7 Summary

With the above literature review in mind, the following factors will need to be addressed in the proposed research, viz.:

- **Strength and hardening of cement paste:** Cement paste sets and hardens with time, which can produce a robust core body.

- **Hydration of cement:** The hydration of cement paste produces calcium hydroxide by chemical means, which on heating converts to calcium oxide. On hydration, the calcium oxide swells with a disruptive action that can break up a core body that is not too robust after having been fired.

- **Failure of concrete under fire**: Cement paste with an aggregate of silica, cracks and loses strength after being fired, which can act as an aid in the disintegration of a core body.

- **Spalling:** it is the disintegration that occurs in cement after the cement has been subjected to a fire.

- **Binding properties:** Cement posses good binding properties as is generally noted when cement is mixed with aggregate. The gel in the cement paste binds with the added aggregate to form a strong mass.

1.4.8 Binders and quick-setting agents

Binders are required in core formulations to hold the powder and aggregate ingredients in a firm mass prior to firing. In this context, both plaster and cement may be regarded as binders.

1.4.8.1 The properties of plaster as a binder

Plaster of paris will be studied as a material that can add possible advantages to the development of a disintegrating core. Plaster of paris has been extensively used in cores (cf. 1.1.5) but has been limited to the low temperatures of core baking at around 600^0C. In this study, plaster of paris will be raised to between 900^0C and 1000^0C, which is the sintering temperature required for the ceramic shell to form a refractory and robust structure.

Plaster of paris, as a binder, is a basic ingredient of the luto investment technique as well as most traditional core bodies. In this context, Groover (1996: 271), introduces the merits of plaster mould casting:

> *Plaster mold casting* is similar to sand casting except that the mold is made of plaster of Paris ($CaSO_4$-$^1/_2H_20$) instead of sand. Additives, such as talc and silica flour, are mixed with the plaster to control contraction and setting time, reduce cracking, and to increase strength. To make the mold, the plaster mixture combined with water is poured over a plastic or metal pattern in a flask and allowed to set… The fluid consistency permits the plaster mixture to readily flow around the pattern, capturing its details and surface finish. Thus, the cast product in plaster molding is noted for these attributes.

Plaster of paris that is typically used in core formulae (cf. Allen and Kolbe 1.1.5) usually has soft firebrick added to reduce shrinkage, reduce cracking and to increase strength. Talc and crushed firebrick due to their inert characteristics to fire, have no positive contributing properties that can aid in the disintegration of the core after firing and will not be considered in formulating a disintegrating core. Silica sands (discussed in more detail below), on the other hand, have the inherent property of thermal expansion and contraction at 573^0C – 575^0C, which could aid in the disintegration of a core, as well as providing strength and the control of shrinkage in a formula that contains plaster of paris as well as providing porosity to the core.

Ammen, (1980: 15), states that:

> Plaster mold casting has a number of applications. The method is a variation of sand casting. Instead of using sand to make the mold a mixture of plaster, talc and water flow up around the pattern. After the plaster has set, the pattern is withdrawn. The mold is then baked in an oven, driving off moisture. This process is more expensive than sand casting, but it does offer a higher degree of dimensional accuracy.

Dimension stability is an important factor in art bronze casting, as replicas of models should be reproduced as accurately as possible. Cement shrinks as it is heated and silica has a volume increase at 573^0C. The addition of plaster of paris to a mixture containing cement and silica in a core formula could add dimensional stability to the mix.

Groover (1996:271) confirms that the curing of the plaster mould is one of the disadvantages of the luto process, at least in high production, because the mould has to be baked for several hours to remove moisture. Even with the baking, not all the moisture content is removed from the plaster. The dilemma faced by foundry men is that mould strength is lost when the plaster becomes too dehydrated, and yet moisture content can cause casting defects in the product. A balance must be achieved between these undesirable alternatives. Another disadvantage with the plaster mould is that it is only slightly permeable, thus limiting escape of gases from the mould cavity.

According to Groover (1996:271) this problem can be solved in a number of ways:

- Evacuating air from the mould cavity before pouring.

- Aerating the plaster slurry prior to mould making so that the resulting hard plaster contains finely dispersed voids.

- Using a special mould composition and treatment known as the “Antioch process” – a process which according to Groover, involves using 50% sand mixed with plaster of paris and then firing the mould in an “autoclave” (a oven that uses superheated steam under pressure cf. Groover, 1996: 271). The result of using this technique is a plaster mould that has superior permeability.

As has been referred to already, plaster moulds cannot withstand the same high temperatures as sand moulds. They are therefore limited to the casting of lower melting point alloys, such as aluminium, magnesium, and some copper-based alloys. However plaster of paris will be investigated as an ingredient in core formulae that will be tested for self-disintegrating properties as it will surely contribute to the formula and setting properties.

Taylor (1964: 316) points out that gypsum (calcium sulphate with two molecules of water as apposed to plaster of paris which has only half a molecule) is effective as a retarder of “flash set” because it reacts with calcium aluminates to produce “either of two practically insoluble complex compounds: calcium aluminate trisulphate hydrate and calcium aluminate monosulphate hydrate.” The formulae for these respective compounds may be expressed chemically as follows: $3CaO.Al_2O_3.3CaSO_4.32H_2O$ and $3CaO.Al_20_3.CaSO_4.12H_2O$.

Gypsum is included in cement as a product that slows the sudden “flash set” of pure cement. Plaster of paris is also used as a binder and as a setting agent in traditional cores bodies used in the luto method. Plaster of paris and cement will both be experimented with as materials in core formula compositions in the search for a disintegrating core body. Both these materials should offer binding properties as well as reduced strength with an increase in temperature.

Hamer (1983: 226) indicates all relevant facts about plaster of paris that cognizance should be taken of, as illustrated in the following table:

Table of plaster mixes

Parts by weight of water	plaster	Minutes pouring time	Further setting (minutes)	% absorbency	Use
100 91	110 100	6	13	50	Patching moulds
100 83	120 100	5,5	18	45	Absorbent bats; hump moulds
100 77	130 100	5	20	40	Casting moulds; jolley moulds
100 71	140 100	3	18	35	Case moulds

Table 1.2 A chart of plaster of paris mixes.

The values illustrated in the table above will be taken into account in future formulae mixes that involve the inclusion of plaster of paris in composite core mixes. Cement and plaster of paris both give stronger dried products when used with the minimum of water as specified in the literature. In future composite experimental mixes containing cement and plaster of paris in combination with, for example silica; the water content will be dictated by the required fluidity that is necessary for the mix to flow into all the extremities of a hollow wax mould.

1.4.8.2 The setting of plaster of paris

In 1.4.7.6 the shrinkage of cement was discussed as this factor may have a bearing on the formulation of future core bodies. Similarly if plaster of paris is used as a quick setting agent in future formulae development, then the setting and shrinkage parameters need to be noted.

Lea (1970: 251), discusses the expansion of gypsum and plaster as follows:

> Taking the specific gravity of hemihydrate at 2.75 and the dihydrate as 2.32, it can be calculated that the setting time is accompanied by a contraction of about 7% of the initial volume of plaster and water. This seems at first sight contrary to

> experience, as the utility of plaster in the preparation of casts is known to depend on its power of filling a mould by expansion and of taking a sharp impression of its surface. But it may well happen owing to crystal thrust that, though the total volume of solid and water present decreases, the effective space taken up by moist mass of interlocking crystals is actually increased while cavities are left in the interior. The overall expansion of plaster mass on setting is about 0.5 per cent. It can be modified by the presence of retarders or accelerators.

This expansion property of plaster of paris may be beneficial in a composite core mix with cement by ensuring that the wetted core mix completely fills the hollow wax model being prepared for casting.

This is confirmed by Hamer (1983: 225), who states that when water is added to powdered plaster of paris, crystals begin to “form and interlock in the setting plaster of paris with an overall expansion taking place. This continues through the first 24 hours. It is only 0.4%.” Here, the heat generated by the crystallization takes up to 30 minutes from the time of mixing.

Neville (Bogue, 1955: 477) noted that the “initial set” of plaster of paris took place before any significant development of heat had taken place. In this regard, the hydration of the plaster proved to be an exothermic reaction:

$$CaSO_4.1,5H_2O + 1,5H_2O \longrightarrow CaSO_4.2H_2O + 3900 \text{ calories}$$

Bogue (1955:477) explains that the “initial set” of plaster occurred before the hemi-hydrate began to hydrate. “Thus it seemed that the set was due to an adsorption of water with the formation of a gel rather than a chemical reaction with water to form the hydrate. After the gel is formed, hydration and crystallization take place.”

As with cement paste, which also exhibits an exothermic reaction, plaster of paris in combination with cement paste should not affect the microcrystalline wax (from which the hollow model is invariably made at the PET) as the melting temperature of microcrystalline wax is close to that of boiling water. Fortunately the core is on the inside of the wax mould so any disfigurement of the wax that may possibly occur due to these exothermic reactions should not reflect upon the outer surface of the wax mould.

1.4.8.2 Summary

The reason for the possible inclusion of plaster of paris in experimental core formulae is to promote quick-setting and binding properties for the pre-fired core mix.

The inclusion of plaster of paris in future core formulations may be considered for the following reasons:

- **Binding properties:** Plaster of paris has good binding properties and the inclusion of either silica or calcium carbonate or calcium hydroxide in moderate amounts, should not weaken this properly unduly.

- **Rapid setting:** Plaster of paris has the property of setting rapidly. This property can be delayed by the addition of other ingredients as well as the quantity of water that is added to the mix.

- **Effect on damp cement paste:** Excess plaster of paris, weakens the structure of damp cement paste. This could also be an advantage if cement paste is added to a core formula mix containing plaster of paris, because the mix will not become too robust as to resist any disintegrating action of the ingredients.

- **Expansion properties:** Plaster of paris has the property of expanding approximately 0,4% on setting, which will be an advantage in filling the hollow wax model completely with the core body.

1.4.9 Aggregates

Aggregates influence the strength of concrete and mortar at high temperature. For this reason alone, they need to be investigated and here, the following authorities have offered valuable insights to this proposed study.

1.4.9.1 Silica sands

The following discussion includes the general aspects of sand added as an aid to binding properties in core formulae, as well as having the characteristics "of a good" filler. Silica and its properties will also be investigated as a possible material for inclusion in a disintegrating core formula.

Hurst (1996: 54) reminds us that silica (quartz) is one of earth's most readily available materials.

Hurst (1996: 54) recorded that the term sand means "a material deposit consisting of grains of average size. Sand grains are classified by sieve sizes and generally speaking, grains of the same average mass tend to be concentrated in the same deposit. "

Grain size used in core formulations has a direct bearing (*inter alia*) on its resultant porosity and permeability (cf. Lomax, 2001).

Hurst summarizes the properties and characteristics of silica sand when used in the casting process as follows:

- **Porous sand:** This is suitable for bronze casting because it has "round grains of a uniform size". Hurst refers to the use in sand casting of a "green sand" which contains "somewhere between 4% to 12% clay." Here, water is also added, to about 4-6% by volume. He also informs us that a simple test for water content is to "squeeze a handful of sand". Here, the moistened sample should hold together and "give a clear impression of the lines of your hand". Here, a good quality moulding sand (cf. Hurst, 1996:54-56) should have the following properties:

    - It should hold together and keep an accurate impression of the cast surface when the model (pattern) is removed.

    - It must be suitably porous to permit any gases to disperse: "too high a proportion of clay will limit porosity".

- "When rammed up with core sand it should resist the pressure of the metal. It should not distort, either when the liquid metal flows into the mould or as the metal is cooling and solidifying."

- The sand should possess suitable refractory properties.

Various particle sizes of silica sand will be investigated as a possible useful refractory in a disintegrating core. Silica sand is both cheap and freely available and makes the choice of this material attractive for this investigation. Brick dust and ceramic grog (chamotte) are both relatively expensive and asbestos is a hazardous material, therefore the latter should not be used.

Hurst (1996: 54-56), describes in his discussion on sand in core formulations that "sharp" sand, as used in the building trade, binds together well to produce a suitable mortar after being mixed with cement. He claims that the shape of the sand grains makes it less porous and consequently less suitable for casting.

Groover (1996: 263), states that the parameters for sand moulds and mould making should have the following properties:

> Foundry sands are silica (SiO_2) or silica mixed with other minerals. The sand should possess good refractory properties, the capacity to stand up under high temperatures without melting or otherwise degrading. Other important features of the sand include grain size, distribution of grain size in the mixture, and the shape of the individual grains. Small grain size provides a better surface finish on the cast part, but large grain size is more permeable. Moulds made from grains of irregular shape tend to be stronger than moulds of round grains because of an interlocking factor, yet interlocking tends to restrict permeability.

The discussion above includes many points of interest that will have to be taken into consideration when deciding what grain size, concentration and the shape of the silica grains should be best suited to a disintegrating core formula.
It is important to know the physical properties of silica as regards its thermal expansion and its possible contribution to the disintegration of a core formula, specifically the

correct silica grain size, shape as well as the concentration of the grains of silica within the formula matrix.

Lea (1970: 657), notes that

> In mortars and concretes the aggregates present undergo a progressive expansion on heating while the set concrete, beyond the point of maximum expansion, shrinks. These two opposing actions progressively weaken and crack the concrete... Quartz, the principal mineral constituent of sands and most gravels… expands steadilly up to 573^0[C].

Here, the transformation from “low” quartz to “high” quartz is described. As is well known (cf. Neville, 1995: 149), at this temperature, quartz undergoes a sudden expansion of 0,85% in volume.

The two opposing thermal properties of concrete containing siliceous aggregates when heated to high temperatures gives a clue to developing a disintegrating core formula. Smith (1963: 285), indicates that even though a siliceous aggregate may be chemically stable, they have major shortcomings with respect to their physical properties at very high temperatures:

> Most striking is the transformation of the quartz crystal from the α to β polymorph at 573^0C (1063^0F) with an increase in volume. At higher temperatures, other internal volume changes occur and the crystal form may be metastable. Furthermore, quartz has a much greater coefficient of thermal expansion than most other rocks up to 600^0C (1112^0F). The consequence in concrete is much greater thermal incompatibility between the cement paste and aggregate and hence greater internal thermal stresses. Many people have ascribed a greater tendency to spalling for these reasons, in particular, the crystal form transformation.

Britannica, Macropaedia (1994: 199), states that high quartz (β-quartz) is more symmetrical at about 573^0C at 1 atmosphere [i.e. it is pressure sensitive] than *α*-quartz.

This expansion, which has a disruptive action on any concrete in which quartz forms an aggregate, will obviously need to be considered in any experimentation involving cement. The experiments that will be conducted in this investigation will be at one atmosphere pressure so this pressure consideration need not be factored into future experiments in this investigation.

For example, the inclusion of the various grades and particle sizes of silica in future core experiments to promote the phenomenon of disintegration in a core after having been fired to between 900^0C and 1000^0C are as follows:

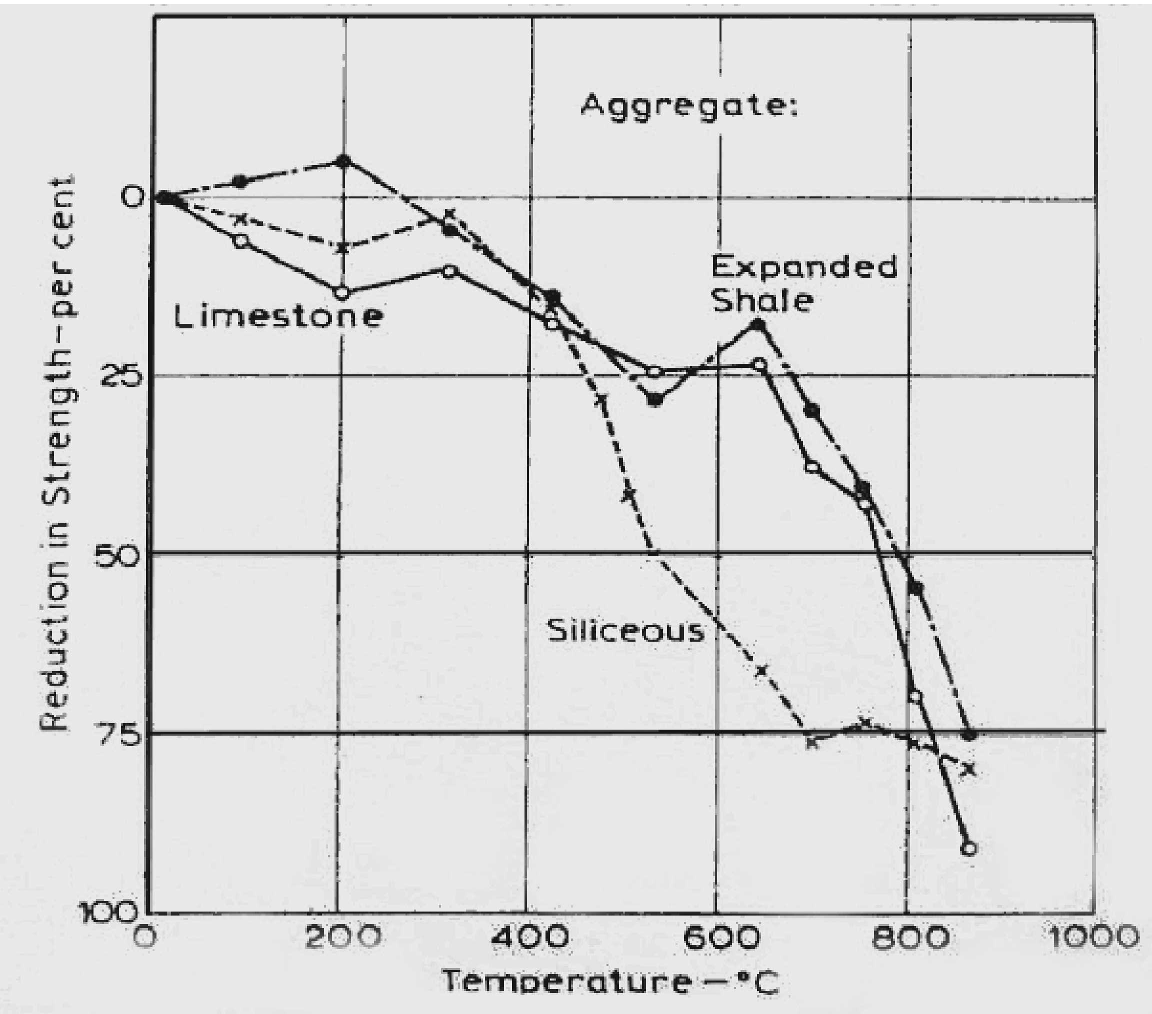
- Silica undergoes a thermal expansion and contraction at 573^0C on being heated and cooled respectively.

- The more rounded shaped silica particles versus stiletto shaped silica grains should aid in the disintegration of a core formula by the very nature of their shape. It is a well-known fact that sharp edged grains compact far more tightly than rounded shapes which implies that the rounded silica grains will provide a less tightly bound structure.

Neville (1995:388) tells us that this type of aggregate influences the response of concrete to high temperature. The loss of strength is considerably lower when the aggregate does not contain silica, for example, with limestone, basic igneous rocks and particularly with crushed brick and blast furnace slag. Neville goes on to say that at temperatures above 430^0C siliceous aggregate concrete loses a greater proportion of its strength than concretes made with limestone or lightweight aggregates but, once the temperature has reached some 800^0C, the difference disappears.

This is important if one considers that a number of aggregates will be added to the cement during testing including plaster, chamotte, silica, calcium carbonate etc.

Neville (1995: 390) indicates by means of a graph the loss of strength of different concrete aggregate mixes when subjected to heat. The phenomenon that takes place here will be taken cognizance of when formulating core bodies that are intended to disintegrate at temperatures of between 900^{0}C and 1000^{0}C (cf. Young and Fennel, 1986: 111).



Graph 1.1 illustrating the loss of strength of limestone, expanded shale and siliceous concrete subjected to a final temperature of 871^{0}C,reproduced from figure 8.19 "Reduction in compressive strength of concrete heated without application of load and then tested hot; average initial strength of 28 MPa (4000psi) $^{8.108}$ " (Neville, 1995: 390).

It is well known that aggregates as used in concrete seldom display shrinkage. However, according to Neville, the range of behaviour during thermal expansion is quite varied and often complicated by phase changes. As has already been mentioned, the quartz inversion phase or physical decomposition of the aggregate (e.g. especially limestone) which occurs at high temperatures.

It is also very important to know how the aggregates are affected by fire and Crozier and Sanjayan (1999: 18-19), explain concisely this effect of fire on aggregates. They state that

> The type of aggregate has a significant influence on the fire resistance of concrete. It is well known that the strength of normal weight concrete depends more on the bond between aggregate and the cement paste than on the strength of the aggregate itself. However, at elevated temperatures, the bond is damaged due to differential expansion of the aggregates and cement paste. Thus the thermal expansion of various rocks is a very important piece of information, particularly where thermal compatibility between the aggregate and the cement is concerned. At room temperature, the coefficient of thermal expansion for most rocks is lower than that of the cement paste and this differential expansion causes damage in concrete at low temperatures (room temperatures).

Crozier and Sanjayan, (1999: 19), further comments on aggregates in cement influenced by temperature.

> From the viewpoint of fire resistance, granites are the least favourable aggregates. They undergo inordinate amounts of expansion between 650^0C and 800^0C. In contrast, anorthosites appear to be ideal by virtue of their petrochemical stability and lower thermal expansion (only 1% at 950^0C).
>
> Quartz, by virtue of its relative abundance in the earth's crust (approximately 12%), is a widely used aggregate in concrete. Among its crystalline forms, α-quartz is the most stable at room temperature. At 575^0C, it undergoes a polymorphism inversion and becomes β-quartz. The inversion is accompanied by a sudden expansion (amounting to 0.86% by volume) which severely disrupts the concrete. Although unfavourable, this is not much worse than most rocks, given that the cement paste matrix shrinks on heating and is badly cracked at 575^0C, irrespective of the aggregate type.

As cement and silica alone may not produce sufficient disintegrating properties in a core formula, other materials will have to be added to achieve this effect, which will in turn alter the water content that is required to produce an ideal concrete mix.

Neville (1995: 174) has noted that the larger the aggregate particle the smaller the surface area to be wetted per unit mass. He explains that by “extending the grading of aggregate to a large maximum size lowers the water requirements of the mix, so that, for a specified workability and cement content, the water/cement ratio can be lowered with a consequent increase in strength.”

1.4.10 Chemically active fillers

By definition, a filler could refer to any additive other than an aggregate which by virtue of its small particle size merely adds bulk to the cement mixture. For practical purposes a filler is normally made up of particles which appear as a powder to the naked eye. Although this is perhaps a grey area, for the sake of this investigation, an aggregate may be deemed to be a filler when its particle size is equal to or less than 74 microns ().

This review, however is concerned with fillers that are not inert but contribute to the mechanism of cement spalling at high temperature (i.e. above 825^0C).

1.4.11 Calcium carbonate and calcium hydroxide

Calcium carbonate as well as calcium hydroxide will be investigated as possible materials to be included in a core formula with disintegrating properties. Calcium carbonate forms an oxide at a relatively high temperature (cf. Hamer, 1983 :339), which in turn is hydrated when exposed to humid air. As a point of interest, magnesium carbonate (cf. Hamer, 1983:342) also displays similar characteristics but the availability of calcium carbonate is more freely available as “whiting”, which is used extensively in industry. The core formula to be developed is to be a practical one, so ingredients that are generally inexpensive and freely available will be the materials of choice.

Calcium carbonate also plays a part in the decomposition reaction in cement when subjected to high temperatures. This calcium carbonate (6%) is an added ingredient in PPC CEM 11 / A-L 32.5 Portland limestone cement (an extender), which is manufactured in Port Elizabeth (cf. 1.4.7.1).

- **The action of heat on calcium carbonate**

Hamer (1983: 44), states that calcium carbonate is stable and insoluble in water. Calcium carbonate decomposes at 825^{O}C to give calcia (calcium oxide) and carbon dioxide:

$CaCO_3$ at 825^{O}C $\longrightarrow$ $CaO + CO_2$

Holderness (1964: 389), noted that the action of heat on calcium carbonate when heated gives a reversible reaction being:

$CaCO_3$ at 825^{0}C $\longleftrightarrow$ $CaO + CO_2$

However if water is added to calcium oxide it converts to calcium hydroxide. This forms one of the key reactions to a possible self-disintegrating core formula.

Lea (1970: 657), states that limestone (calcium carbonate) “expands steadily until a temperature of about 900^{0} [C] is reached and then begins to contract owing to the decomposition with the liberation of carbon dioxide.”

The addition of calcium carbonate to experimental core formulations should theoretically be converted to calcium oxide above 825^{0}C (Hamer, 1983: 44). On cooling, the calcium oxide absorbs water from the atmosphere forming calcium hydroxide, which expands to “dust”. This phenomenon of dusting could be a contributing factor to the development of a disintegrating core.

- **The properties of calcium hydroxide and calcium oxide**

Lea (1970: 30), states that the product of hydration of lime (Calcium Oxide) by water is Calcium Hydroxide and occurs at around 400^{0}C.

$CaO + H_2O \longleftrightarrow Ca(OH)_2$

Lea further reports that hexagonal plate crystals of calcium hydroxide can be observed in set Portland cement. Calcium hydroxide reacts with carbon dioxide to form calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Bogue (1995: 621), states that “[t]he general structure of cement paste after 28 days hydration is shown… to contain 40 per cent C_3S, 31 per cent C_2S, 6 per cent C_3A and 13 per cent C_4 AF. “ This statement must have the following proviso added in that a cement composition after 28 days of hydration is not a fixed quantity of each phase, but depends on the initial composition of the cement. Bogue concludes that the quantity of $Ca(OH)_2$ liberated is some 10-15%.

This shows that the addition of calcium carbonate will hopefully be disruptive and will assist in the attainment of a disintegration effect. Here, Neville (1995: 387), notes that one of the “changes which occurs as the temperature [of concrete] rises to above 400^0C … is the decomposition of calcium hydroxide so that lime is left behind in consequence of drying. If, however, after cooling, water ingresses into concrete, the re-hydration of lime can be disruptive; thus the damage manifests itself subsequently to the fire.” This reaction in cement gives it the advantage of being a binder in the pre-fired formula as well as a providing disintegrating properties after the cement has been heated above 900^0C in that some of the original $Ca(OH)_2$ formed in the cement paste is converted to CaO and on hydration the CaO should provide disintegrating properties, which further strengthens the reason for including it in test core formulations that are required to disintegrate.

The discussion above further lends itself to the idea of including calcium carbonate or calcium hydroxide into a core formula, especially one that will be sintered to between 900^0C and 1000^0C, as this temperature is a prerequisite to the formation of the ceramic shell investment mould.

Holderness (1964: 386), states that the properties of quicklime (calcium oxide) are as follows:

“Pure quicklime is an amorphous white solid, though, as manufactured, is usually in somewhat discoloured lumps. It is highly refractory, sustaining a temperature of about 2600^0C without decomposition, and then fusing.”

The action of quicklime with water is noted by Holderness (1964: 387), as follows: “if cold water is added to quicklime, there is a hissing and the material swells, cracks and crumbles to a white powder, *calcium hydroxide* or *slaked lime*, with much steam evolved…It is strongly exothermic (15,900 [calories] evolved per gram-molecule).”

$$Ca^{++}.O^{--} + H_2O \longrightarrow Ca^{++}(OH^{-})_2$$

The refractory property of quicklime could be a beneficial property in a cement based core formula by helping to provide a refractory facing the molten bronze.

The reasons for the inclusion of calcium carbonate or calcium hydroxide in experimental core formulations to promote disintegration of the core body after firing in a kiln are as follows:

- The action of the carbonate in a core formula after sintering produces a core that is more porous due to the decomposition of calcium carbonate to the oxide, having a weight loss of 44% (cf. Hamer, 1983: 339).

- The action of the hydroxide in a core formula after firing produces a core that is less porous than that produced by calcium carbonate as the weight loss due to decomposition is only 26.3% versus 44% for the carbonate (cf. Hamer, 1983: 339).

- The oxide forms from either the carbonate or the hydroxide after sintering and reconverts to the hydroxide with a disruptive effect due to between 56% molar to 74% molar percent increase in volume.

- The refractory nature of calcium oxide formed in a core formula after firing would be to provide an additional positive contribution to a core formula, by being able to resist the effects of molten bronze.

1.4.11 Water

Water will be used to make a pourable mass (cf. Definition of Terms 1.10.4) from the ingredients that will constitute a suitable core formula. De-ionized water (cf. British Pharmacopoeia, 2000:1594) will be used throughout the development of a disintegrating formula for the following reasons:

- To standardize the quality of water used.

- To ensure no impurities from local water (Municipal water may affect the results for these and future experiments) (BPB Product Data Sheet. 1995. Standard Plaster (PS040).

- To comply with the requirements of the water to be added to plaster of paris requires water to be as pure as possible. (BPB Product Data Sheet. 1995. Standard Plaster (PS040). However it should be noted that impurities in water can actually assist the hydration of plaster of paris.

1.4.12 Relative Humidity

The effect of water in the form of water vapour in the atmosphere on calcium oxide in experimental test cores will influence the conversion of calcium oxide to calcium hydroxide, with an expansion in volume, which could be disruptive in the test core formulae. The calcium oxide will owe its presence in the test formulae due to the contribution of either calcium carbonate or calcium hydroxide as well as that formed in the hydration of cement upon curing and conversion (cf. Lea, 1970: 657) when fired to between 900^0 and 1000^0C.

Different humidity environments will have to be considered to evaluate the effect that different concentrations of water vapour may have on the disintegration of the core mix.

A R H C apparatus with the dimensions of 400 mm x 400 mm x 400 mm (cf. definition of terms 1.10.6) will be used as a control to stabilize the temperature and relative humidity to a degree (within the parameters prevailing at the time) during the disintegrating tests. The ambient temperatures in Port Elizabeth can vary in one day from a high of 31^0C to a low of 5^0C with a relative humidity variant of 100% in foggy weather to 50% on a dry day (cf. information supplied in consultation with the South African Weather Services at the weather station at the Port Elizabeth airport).

1.4.13 Temperature considerations for fired core formulations

Temperature is one of the various factors that will have to be considered when developing a disintegrating core body. The properties of the five materials that have been chosen as possible ingredients that could contribute towards the disintegration of a core body have been briefly discussed above. The temperature reactions of those findings are summarized as follows:

- Industrials plasters are non-combustible. With a coefficient of thermal conductivity (k0 of 0,5 to 4,0, depending on the density, these materials provide a degree of fire resistance. When exposed to heat, they do not exceed 1000c until three quarters of the chemically-combined water is driven off. At 9820C the CaSO4 portion dissociates into quicklime, sulphur dioxide and sulphur trioxide (cf. United States Gypsum Company 1989: 4).

- Silica: It is stable at 900^0C to 1000^0C. It changes from α- quartz to β- quartz at 575^0C (cf. Crozier and Sanjayan, 1999: 19). This expansion and the converse shrinkage of cement may contribute to the disintegrating properties of a formula containing these two ingredients.

- Calcium carbonate: All authorities agree (Holderness, 1964: 389; Hamer, 1983: 44 etc.) that the decomposition of pure calcium carbonate begins at 825^0C and converts to calcium oxide and carbon dioxide. However, the calcium carbonate used in this investigation contains 95% $CaCO_3$ and 4% $MgCO_3$ which upon analysis revealed a disintegrating eutectic temperature of 730^0C.

- Calcium hydroxide: The decomposition of calcium hydroxide into calcium oxide and water occurs at about 400^0C at one atmospheric pressure (cf. Lea, 1970: 30). This temperature is well within the limits of the temperatures intended for sintering the ceramic shell. Hydrated lime may present a better option as an addition material to a core mix than calcium carbonate due to its lower conversion temperature to calcium oxide, but this will only be a determined in future experimental tests.

- Cement: Portland cement is notably weakened when exposed to temperatures above 600^0C and undergoes major structural damage above 900^0C (cf. Lea 1970: 658).

- The combined ingredients that go into making a disintegrating core-body must withstand the heat of the molten bronze at 1200^0C to ensure that the integrity of the outer bronze surface is not compromised by the degradation of the disintegrating core-body during this process.

The relationship that exists between the individual materials discussed in the literature review and the parameters of shrinkage, refractory parameters, porosity, temperature, humidity, formula water content, and the post-fired robust nature of the sintered core will all have to be taken into consideration in the formulation of a successful disintegrating core.

1.5 METHODOLOGY

1.5.1 Preamble to the methodology

The methods investigated in the literature review regarding the disintegrating core do not give any definite clues as to how a disintegrating core can be developed for use in conjunction with the ceramic shell mould process.

Perhaps the phenomenon of heat degradation (cf. Lea 1970: 657) that occurs in concrete and mortar after being subjected to a fire can be used as a clue in the development of a disintegrating sacrificial core (cf. glossary). Following this lead, as a point of departure for the purposes of this investigation, test samples of cement (cf. glossary) mixed with sufficient de-ionized water to form a paste, which will be poured into a silicone rubber mould 100 mm x 20 mm x 20 mm. After seven days of curing (to coincide with the general time taken to invest a wax model in a ceramic shell) the samples will be subjected to temperatures of 945^{0}C (cf. glossary: sintering temp of the ceramic shell) to evaluate the effect that this temperature has on pure cement.

Incremental amounts of different materials that have the perceived potential to contribute to the spalling phenomenon will be introduced into the cement mix and subsequently fired to 945^{0}C (delimitations 1.6.9, empirical method). This analogy will be progressively followed to the extent where possible values of the contributing materials in the cement could give improved results in the disintegrating or spalling process.

These results will in turn be applied to the investigation as to a possible solution in producing a sacrificial core with disintegrating properties that meet the following criteria:

- The sacrificial core should be refractory to molten bronze at its pouring temperature at approximately 1200^{0}C (cf. literature review 1.4.5.1 and 1.4.7.6).

- The sacrificial core after being poured into a wax mould should be sufficiently robust after seven days to withstand the rapid rise in temperature from room temperature to approximately 600^{0}C during the de-wax process and then the steady increase in temperature in the sintering kiln 945^{0}C (cf. literature review 1.4.3).

- The sacrificial core must be sufficiently porous to allow for the escape of residual water (cf. literature review 1.4.6), contained in the core mix, during the rapid rise in temperature that occurs in the de-waxing process and in the sintering of the ceramic investment.

- The sacrificial core must be mechanically robust to withstand being suspended by the aid of holding pins, inside the mould and to resist the sudden weight of molten bronze flooding the mould cavity during the bronze pour (cf. literature review 1.4.3).

- The core should begin to disintegrate after being fired to between 900^{0}C and 1000^{0}C within a specified period of time (cf. delimitations 1.6.5).

Considering the factor of any residual water remaining in the wetted sacrificial core, it is understood that cement will have to be further manipulated if it is going to be used successfully in a sacrificial core, due to its inherent property of retaining water in its microscopic pores (cf. pore pressure, def. of terms 1.10.5) which could lead to the production of steam and the subsequent possibility of a steam explosion in the core. A practical parameter of the sacrificial core requires that it be poured into the mould and should be ready to be fired within about a week (practical considerations used in the PET sculptural studio), which is the time taken to build the outer ceramic shell investment around it. It is assumed at this stage that the use of cement as a major constituent in a core formula will thus be reduced, due to its water retention properties, although the binding properties could be advantageously used in some manner still to be determined.

The nature of the core material that will satisfy the parameters stated above will have to be determined in a practical way as there is no definitive mould formula (cf. N. Allen, D. Jones and P. Kolbe, paragraph 1.1.5) that can be used as a starting model. The formulae used for sacrificial cores at the PET that have been investigated, have been made on an ad hoc basis over time, and there appears to be no documented information pertaining to exact quantities or qualities of materials used in these core formulations. However these different formulae have proved to satisfy the core parameters detailed above, (except for the disintegrating factor) and the nature and physical characteristics of these cores will have to be further studied to determine whether they can be incorporated with any additional beneficial contribution that already has been obtained in preliminary cement investigations with reference to disintegrating factors.

The general characteristics of the N. Allen, D. Jones and P. Kolbe (cf. paragraph 1.1.5), cores are that they are structurally open bodies composed mainly of crushed refractory brick and bound with a small quantity of plaster of paris. The crushed refractory brick is extremely porous by nature and the brick and plaster of paris presents a structure that is structurally strong, refractory and resistant to sudden changes of temperature applicable to the ceramic shell process. Further to the core formulae produced by N. Allen, D. Jones and P. Kolbe, the basic core formula described by Mills (1990:120) will also be considered in the development of a disintegrating core due to its basic composition of having only two components in its formula.

1.5.2 The core formula described by Mills (1990: 120), is as follows:

Plaster of paris	1 part
Grog (ground ceramics)	3 parts

It must be noted that the above formula does not describe the type of plaster of paris or the characteristics of the crushed brick used in the formula. It will also be taken into consideration that the core formulae studied to date do not include specific parameters for the cores but leave these as idiosyncrasies to the discretion of the individual core fabricator.

1.5.3 The approach to the methodology

The approach to the problem in the methodology (a process-oriented technique using empirical methods) will be to display a pathway that is to be followed by the way of a series of incremental steps. These steps will illustrate the basic concept of the investigation with explanatory notes, giving the reasons for the different steps envisaged to reach the goal of a disintegrating core. The cement correlation in conjunction with plaster of paris as a comparative material will be followed in the pathway with each step ending in positive or negative attributes that can perhaps be used to determine the parameters for a disintegrating core formula which ultimately conforms to all defining characteristics spelled out in 1.1.4.

1.5.4 The pathway for the development of the disintegrating core formulae

1.5.4.1 The first step

The first step in the investigation will be to determine the spalling (cf. def. of terms 1.10.5) properties of hardened pure cement paste, the effect of plaster of paris and the effect on a mixture of cement and plaster of paris that has been fired to 945^{0}C. When plaster of paris is included in a Portland cement and water mixture, e.g. in a mortar, an adverse reaction can occur. This phenomenon will be investigated as it may have a direct bearing on the final performance of the core formula. The volume of water will be kept at an amount that is just sufficient to produce a pourable mass.

1.5.4.2 The second step

The second step in the process will be to determine the effect that plaster of paris has on the formula when mixed with either silica 0.074 mm, silica 0,2 mm and silica 0,95 mm and fired to 945^{0}C.

1.5.4.3 The third step

The third step will be to determine the combined effect that cement has when mixed with either silica 0,074 mm, silica 0,2 mm and silica 0,95 mm and fired to 945^{0}C.

1.5.4.4 The fourth step

The fourth step will be to determine whether powdered calcium carbonate will affect the fired characteristics of cement or plaster of paris when heated to 945^{0}C.

1.5.4.5 The fifth step

The fifth step will be to determine the combined effect of plaster of paris, cement and either silica 0,074 mm, silica 0,2 mm or silica 0,95 mm when fired to 945^{0}C.

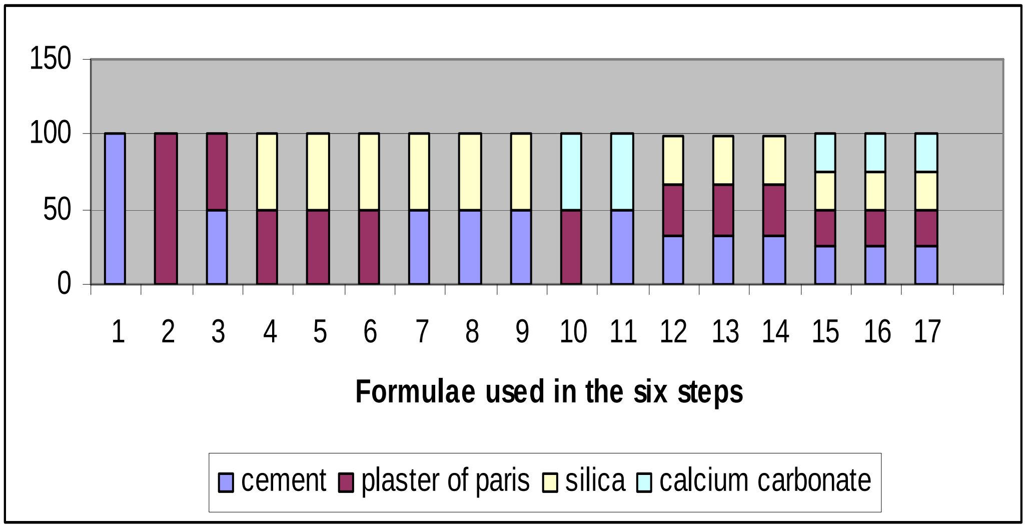
1.5.4.6 The sixth step

The sixth step will be to determine the characteristics of an equal mixture of plaster of paris, cement, calcium carbonate with either silica 0,074 mm, silica 0,2mm or silica 0,95 mm when fired to 945^{0}C.

1.5.4.7 The seventh step

The seventh step will be to evaluate the parameters obtained in the six steps above and to formulate further pathways that could lead to the determination of a successful disintegrating naked core (as discussed in the background to the problem 1.1.5).

The bar chart below, as a point of clarification only, shows how the different formulae mixes derived from the six steps designated above will be illustrated to present a consolidated picture of the formulae core mixes compared to their disintegrating times.



Graph 1.2 A column graph illustrates the 17 formulae compositions used in the six steps for the disintegrating core formulae investigation.

1.5.5 Empirical testing methods

The experiments that will be conducted in the five sub-problems will be of an exploratory nature, and will be conducted in such a manner that the sequential results derived from these tests will be used to indicate the way forward in which the core formulations being developed, should be further investigated. A minimum of three individual tests will be conducted for each experiment being investigated to ensure that the results that are recorded are repeatable (cf. delimitations 1.6.9).

1.5.6 All measurements will be by volume

Volume measurements will be used throughout this investigation when making up different formulae and only when the final formula has been selected will the volume values be converted to mass measurements so that future investigators can accurately measure the quantities that make up the said formula (cf. delimitations 1.6.8).

1.5.7 The materials and the practical methods that will be used for the compounding and the scrutiny of the different formulae mixes that will be made to test the theory of at a disintegrating core material.

- **Selection of materials**

  The different materials selected for use in the proposed formulae experiments have been sourced from the literature review for their possible contribution to the development of a disintegrating core body. The selection of the chosen materials is set out below defining the characteristics of each of the materials.

1.5.7.1 Plaster of paris

The plaster of paris chosen for this study will be from a single 50 kg bag of BPB Gypsum standard code number 1612032002 manufactured by BPB Gypsum Pty Ltd. South Africa (Technical Services, Rhinoboard Division, Telephone 021-9595000 Cape Town (cf. product specification in the appendix VI).

1.5.7.2 Cement

The cement that will be used throughout this investigation will be from a single 50 kg bag of Surebuild cement code CEM 11 / A-L 32,5 Portland limestone cement, manufactured by Pretoria Portland Cement, Port Elizabeth (cf. technical literature in the appendix I).

1.5.7.3 Silica

The various grades of silica that will be tested in the experimental formulae will be 0,074 mm, 0.2 mm and 0,95 mm particle sizes (cf. product specification in the appendices).

1.5.7.4 Silica 0,074 mm

The silica 0,074 mm will be from a single 50 kg bag supplied from the Lafarge quarry located in the suburb of Cotswold in the northern suburb of Port Elizabeth (cf. product specification in the appendix II).

1.5.7.5 Silica 0,2 mm

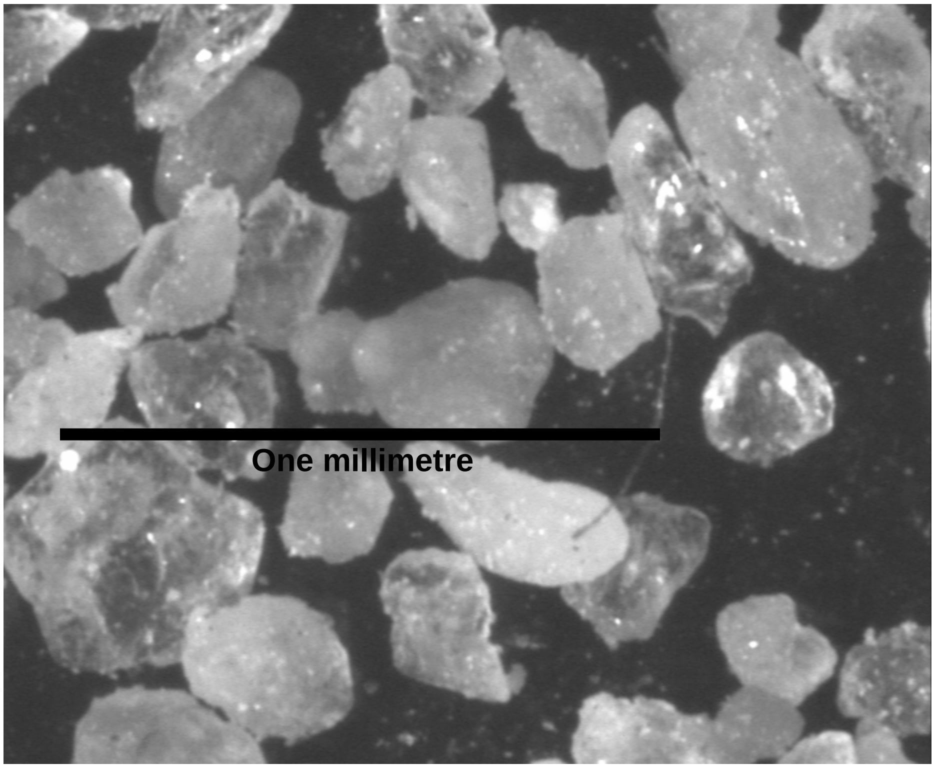


Figure 1.2 A photograph illustrating the sharp shapes of the 0,2 mm graded silica particles. Some of the particles do have sharp edges but the majority of the particles are rounded. The specifications for the silica 0,2 mm are given in the appendix III.

1.5.7.6 Silica 0,95 mm

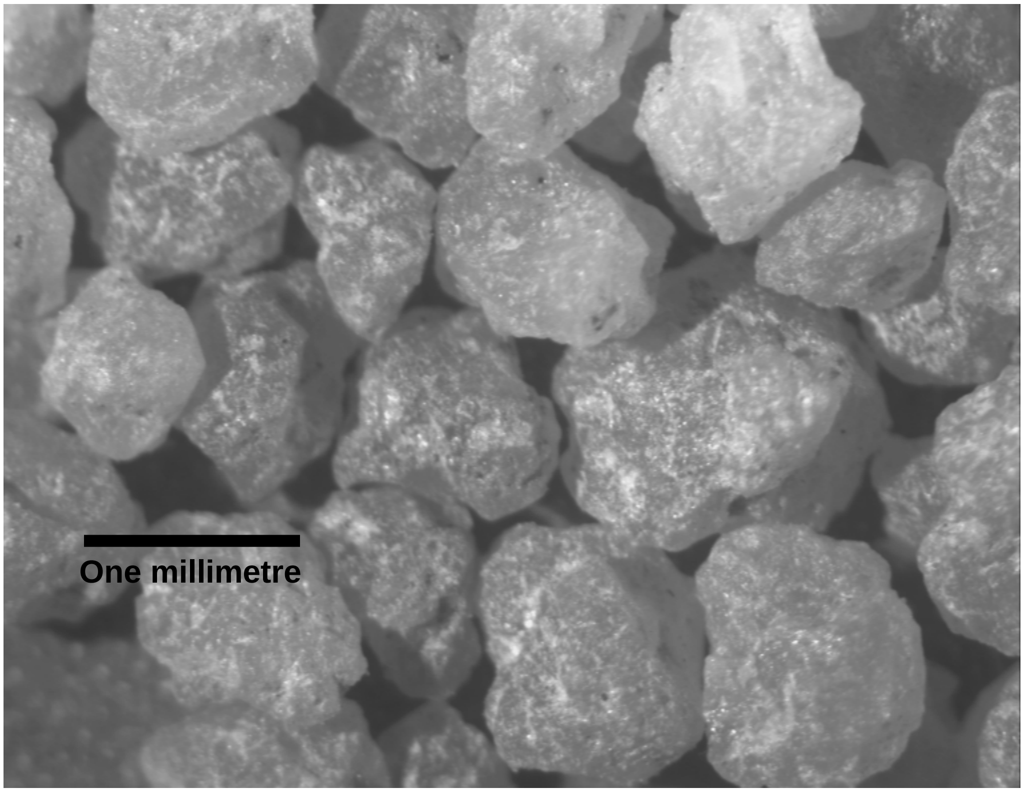


Figure 1.3 A photograph illustrating the more rounded shapes of silica 0,95 mm.

The edges of the silica particles appear to be slightly ragged in appearance, but the general form is a rounded shape. A single 50 kg bag of this product will be used for all the testing in this investigation (cf. product specification in the appendix IV).

1.5.7.7 Calcium carbonate 0.010 mm

The 0.010 mm particle size is produced by Idwala Carbonates under the trade name Kulubrite-10. It is described as white limestone filler with a composition of 95% calcium carbonate, 4% magnesium carbonate and a loss on ignition of 44%, giving a calcium oxide content of 53% and magnesium oxide of 2% (cf. appendix V).

A single 50kg bag of this product will be used for all the tests conducted in the study (cf. product specification in the appendix V).

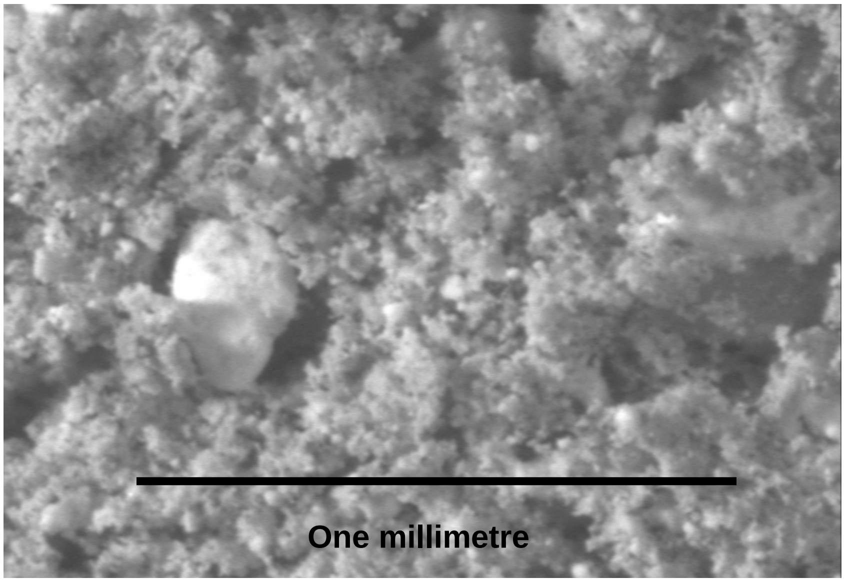


Figure 1.4 A photograph of a 50 x magnification of the powder agglomerations of 0,010 mm particle size calcium carbonate.

Note the amorphous characteristic structure of this calcium carbonate product. A 0,2 mm silica particle is embedded in the powdered calcium carbonate agglomerations as a way of visual comparison.

1.5.7.8 Calcium Hydroxide

Calcium hydroxide is sold under the name of Limbux hydrate lime. It is 95% pure with 2% calcium carbonate and other minor ingredients.

A single 50kg bag of this product will be used for all the tests conducted in the study (cf. product specification in the appendix VI).

1.5.7.9 De-ionized water

De-ionized water will be used throughout the investigation as a wetting agent to make the different test formulae into pourable masses. De-ionized water will serve as a standard for this investigation and is defined as purified water having the following properties: A clear, colourless, odourless, and tasteless liquid prepared from suitable potable water by treatment with ion-exchange materials as specified in the British Pharmacopoeia (2000: 1594).

1.5.8 Design of the silicone rubber mould

A photograph of the silicone rubber mould that will be used to prepare naked test bars has dimensions of 100 mm x 20 mm x 20 mm. The soft wax inserts in the mould are visible in the photograph illustrated below and are used to code the individual bars by indicating the particular formula mix being used.

Figure 1.5 A photograph of the silicone rubber mould showing two naked test bars to the left of the photograph that have been removed from the mould.

1.5.9 Mixing methods, pourable mix, filling the silicone rubber mould and curing time

1.5.9.1 Core material mixing method

All materials will be thoroughly dry-mixed together. De-ionized water will be slowly added whilst the materials are being continuously mixed, using a stainless steel mixing tool until the mix becomes a pourable mix. The volume of water will be thus determined and will be used in all subsequent formulae having similar compositions.

1.5.9.2 Core paste pouring consistency

The amount of de-ionized water as well as the ingredients will be accurately measured by volume using a graduated measuring cup. The amount of water that will be added to produce a pourable mix will be experimentally determined when water is initially added to the various formulae mixes. The degree of fluidity will be referred to be a mix that just flows from a suitable mixing container without having to shake the container to ensure all the mix has been poured out. This will be referred to as a pourable mix.

The time taken for the pourable formula mix to set into a weak but firm mass, usually occurs within 10 minutes after adding the requisite amount of de-ionized water to the mix, and becomes firm mass after 6 hours. At this stage, a wax mould containing the core mass can be invested using the ceramic shell process. The quantity of de-ionized water that is added to the formula to achieve a pourable mass (cf. volumes in table 6.2) is important for three reasons namely:

- If the quantity of water exceeds the values obtained by experimentation (cf. table 6.2) the already wet mixture suddenly becomes very runny and it serves no purpose as this water has to be expelled once again from the core during the de-wax process.

As the factors mentioned above can all produce variable results and it is important that the volume of de-ionized water as well as the volumes of the other ingredients in the mix be carefully and accurately measured to ensure repeatable results can be obtained for the formula mixes.

1.5.9.3 Filling the silicone rubber mould with core paste

The core paste should have a similar consistency for all the paste formulae mixes that are used to make the test bars. The paste mix should be poured into the silicone rubber mould as soon as possible after adding the requisite amount of de-ionized water, due to the setting characteristics of both the cement and the plaster of paris in the formulae where applicable.

The paste mix being poured should be allowed to slightly overfill the rubber mould and the excess paste should then be scraped away using the back of a flat stainless steel knife to ensure that the exposed surface is level with the walls of the mould.

This procedure is a prerequisite for all the test pieces that are going to be used in the transverse breaking strength instrument where a diametrically uniform bar is required for the test.

1.5.9.4 Curing the core material in the rubber mould

The core material should be cured in the silicone rubber and kept in the R H C apparatus to emulate practical conditions that will have to be met later when cores are made in wax moulds for the actual bronze pours. The cores should be allowed to cure for seven days as this is the general time taken to invest a mould in the ceramic shell. The term cured is used as cement will be the basic ingredient in all future formulations (cf. literature review 1.4.7).

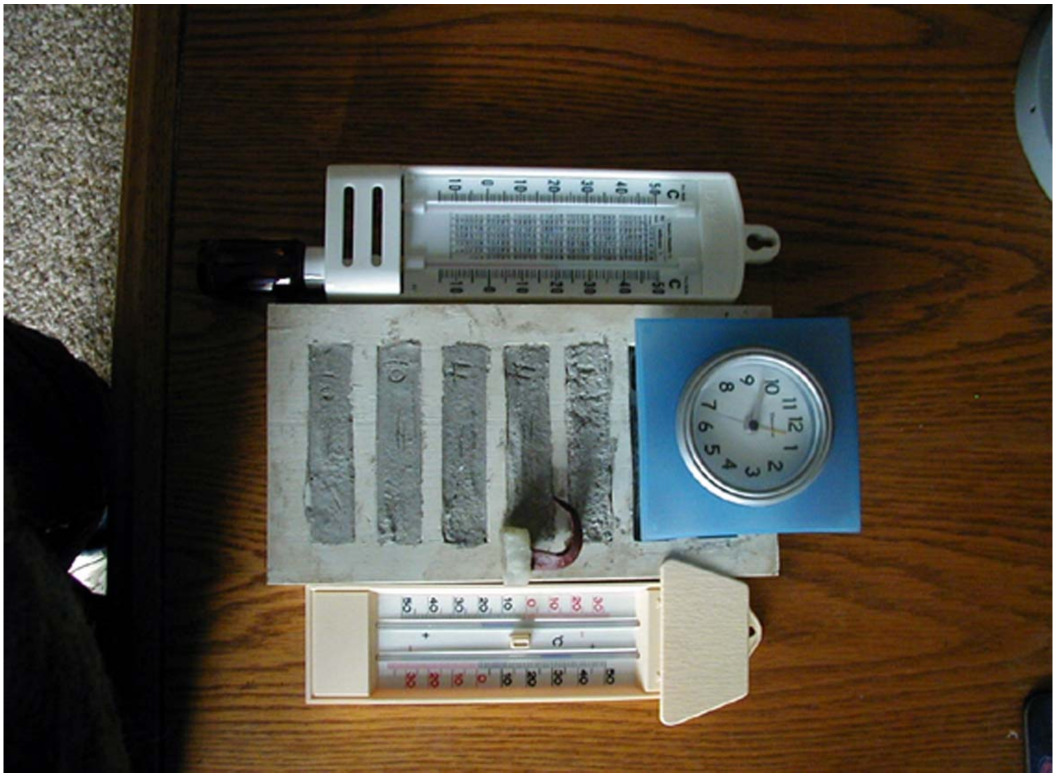


Figure 1.6 A photograph that illustrates how the proposed naked test bars in a silicone rubber mould.

1.5.10 Compression strength determination

The compression strength of the naked test bars under investigation will be tested using the Hounsfield test equipment (S series) to determine the compressive strength of the test bars in MPa (mega pascals).

Procedure:

The test specimens shall be placed in the Hounsfield machine so that the 80 mm dimension is parallel to the support edges (cf. figure 1.7). The computer programme to run the compression test is detailed in Appendix IX.

Figure 1.7 A photograph of the Hounsfield computerized test equipment.The photograph shows how a naked test bar made from a core formula will be tested for compressive strength, which is measured in megapascals (MPa).

The testing of the test formulae in the form of sintered naked test bars is controlled by the computer keyboard and the operation once started for each test is fully automated and controlled by the computer programme. The programme to operate the Hounsfield apparatus may be found in appendix IX.

1.5.11 The shrinkage test

The limits set out in the shrinkage test below, namely 1% or less, where determined to be within art studio foundry tolerances, as discussed with D. Jones, sculptor lecturer at the PET in consultation with G. Detleefs, owner of Ingwe Editions, Koelenhof 7605 South Africa, manufactures and fabricators of fine bronze castings (cf. delimitations, 1.6.10).

1.5.11.1 Measuring the length of the set damp core bar for the shrinkage test

The damp core material that has been poured into the rubber mould should have set and should present a firm surface after six hours. The surface of the test bar can now be inscribed along its entire length with a straight line using a vernier caliper and a sharp needle tool. It will be necessary to demarcate an 80 mm length, by inscribing two short lines at right angles to the original line, and which are exactly 80 mm apart. This marked length will serve as the damp length in the shrinkage determination test for the core body under investigation.

1.5.11.2 The shrinkage test procedure

Shrinkage tests will be conducted on the naked test bars, seven days after making the bars and again after firing to 900^0C, 945^0C or 1000^0C.

Method

A straight line is inscribed along the long axis of the naked test bars and two cross marks are made 80 mm apart. These inscribed lines are made on the test bar six hours after the bars have been poured into the silicone rubber mould and have had sufficient time to set and harden. Using a sharp needle tool and a vernier caliper, an 80 mm demarcated line is inscribed upon the surface of the bar. The test bar is again measured after seven days, just prior to the firing to 945^0C.

The naked test bars will be fired to 945^0C. The length will again be measured and recorded against the original seven day cured length measurement. These measurements will be used to calculate the shrinkage of the naked test bar.

$$\frac{\text{Seven-day cured length — fired length x 100}}{\text{Seven day cured length}} = \text{percentage shrinkage.}$$

Figure 1.8 A photograph illustrating the vernier caliper, which will be used to measure a typical test bar in the test for shrinkage.

1.5.12 Temperature considerations

The fired temperatures at which the naked test core formulae will be tested for disintegrating properties will be 900^0C, 945^0C and 1000^0C (cf. literature review 1.4.13).

1.5.12.1 Temperature and relative humidity controls for the test bars.

The test bars that will be made as illustrated in figure 1.5, will first be fired to either 900^0C, 945^0C or to 1000^0C before the following tests are conducted.

1.5.12.2 Ambient temperatures

The normal outside temperature in Port Elizabeth can vary from 5^0C to 31^0C excluding extremes in the low and top temperatures and the relative humidity can vary from 50% on a dry day, to 100% in foggy conditions (Information supplied by the South African Weather Services at the Port Elizabeth weather office).

The large variation in temperatures and relative humidity values that can occur over a twenty-four hour period of time necessitates that the disintegrating tests be conducted under more controlled conditions of temperature and relative humidity. Three insulated boxes, 400 mm x 400 mm x 400 mm were constructed using Styrofoam insulation panels. A single insulated Styrofoam box will be referred to in the text as the R H C apparatus (relative humidity control apparatus).

1.5.13 Relative humidity

The relative humidity testing will be to determine what occurs to the fired core formulations at low, medium and high relative humidity values. In Port Elizabeth, being a coastal town and the PET being a few hundred metres from the coast shows relative humidity ranges that would obviously be different to those obtained in a town situated inland, but the intention here is to discover what effect relative humidity has on the sintered core formula.

A wet and dry bulb thermometer will be used to record the percentage humidity from the set of tables that are supplied with the instrument. The fired core exposed to different relative humidity conditions could be a controlling factor in the disintegrating times of the test cores and will be investigated in the relevant experiments.

Figure 1.9 A photograph illustrating the interior of the R H C apparatus with dimensions of 400 mm x 400 mm x 400 mm. Naked test bars F21 and F22 (as examples) have been placed on the grid as illustrated, after first having been fired to either of 900^0C, 945^0C or 1000^0C.

The fired bars are subjected to either a humid atmosphere achieved by placing a water trough inside the closed RHC apparatus where the humidity tends to remain at 91% and at around 20^0C or generally close to 81% inside the R H C apparatus with the lid removed. Thirdly, tests will be conducted at a lower relative humidity by placing the fired naked test bars inside the R H C apparatus with the lid removed. This process generally produces relative humidity conditions inside the apparatus at around 73%.

The temperature in Port Elizabeth during March to September to March, when the tests will be conducted hovers around 14^0C to 24^0C inside a room specially set aside away from draughts and direct sunlight. A further set of tests will be conducted regarding the effects on the disintegrating times of the test cores by placing the fired test bars under investigation in a refrigerator having a functioning thermostat to control the temperature at 10^0C, which will be read using an accurate mercury thermometer The test pieces will be protected by placing them in open plastic containers so that they are not wetted by any water within the refrigerator, which will invalidate the tests being observed.

1.5.14 The electric kiln

1.5.14.1 Firing the naked test bars in an electric kiln

The test cores that have been cured for seven days in the silicone rubber mould and placed inside the R H C apparatus with the lid removed are now fired to 945^0C in an electric kiln. The firing speed or the rate of temperature rise from room temperature to 945^0C is approximately four hours.

1.5.14.2 The electric kiln with a soak controller

The temperature controls that will be used to control the rate of temperature rise as well as any soaking period (cf. glossary), will be by an electric full scale digital pyrometer with the necessary electric controls to allow for an automatic switch-off mode when required.

Figure 1.10 A photograph of an electric control instrument which is used to control the temperature of the kiln as well as having a soak control mode that allows the kiln temperature to be maintained at the upper temperature set or a specific firing.

1.5.14.3 Orton Cones

To check the of the firing temperature parameters inside the kiln, an Orton cone (cf. Hamer, 983: 330) is used in conjunction with the electric controller used and discussed above. The principle of the Orton cone, which is the trade name for a slumping pyrometric cone with specific characteristics, is that it reacts actively to the two variables of temperature and time. The designated Orton cones selected for this study are cones 010 (900^{0}C), 08 (945^{0}C) and 06 (1000^{0}C) that bend through 75^0 from a standing position (i.e. 15^0 off 90^0 as indicated in figure 1.11).

Figure 1.11 A photograph illustrating a straight Orton cone standing at 15^0 off 90^0, which is its designated position prior to firing. The second cone has bent, the tip of the cone just touching the base, which indicates the kiln temperature has reached the designated temperature.

1.5.15 Measuring the disintegrating core formulae characteristics that have been made into naked test bars

1.5.15.1 Discussion of the parameters for testing the disintegrating core

There is no official or specific testing procedure to measure the disintegrating characteristics of the test core bars.
The following procedure will be adopted to measure the elapsed time for the disintegration of the test bar:

A grid made from metal rods 1 mm in diameter and spaced 10 mm apart will be used as a base on which the recently naked test bars will be placed directly after being removed from the fired kiln.

A maximum and minimum thermometer as well as a relative humidity thermometer will be placed next to the fired core bars on the grid. These instruments will be read every six hours and the temperature and relative humidity values will be recorded alongside the test bars being tested for their disintegrating potential.

The elapsed time, beginning from when the test bars have cooled to room temperature to the time that the test bars disintegrate and have subsequently fallen through the grating, will be recorded as the disintegrating time.

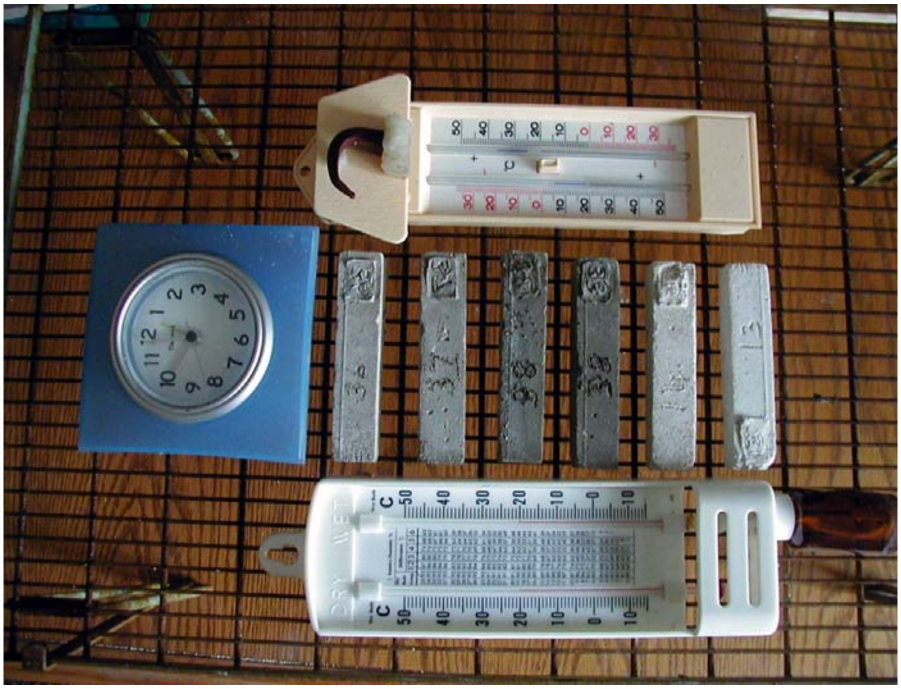


Figure 1.12 A photograph illustrating how the fired naked test bars will be placed on a metal grid after cooling to room temperature.

In figure 1.12 note the close proximity of the maximum and minimum thermometer as well as the wet and dry bulb thermometer. The Orton cone, number 08 is used to verify the temperature of 945^{0}C that was recorded inside the kiln during the sintering process (cf. figure 2.1, chapter 2).

1.5.15.2 Recording the disintegration characteristics of the fired naked test bars over 72 hours (cf. first sub-problem)

The disintegrating characteristics of the sintered naked test bars will be an unknown factor and for this reason it was decided that the naked test bars would initially be monitored at six-hourly intervals. The disintegrating attributes of the core formulae will be recorded in the following tabular arrangement. A six-hourly observation interval has been initially chosen to detect any sudden if unexpected changes in the sintered core over time:

Elapsed time	Temperature	Relative humidity	Test core	Test core	Test core	Test core
6 hours						
12 hours						
18 hours						
24 hours						
30 hours						
36 hours						
42 hours						
48 hours						
54 hours						
60 hours						
66 hours						
72 hours						

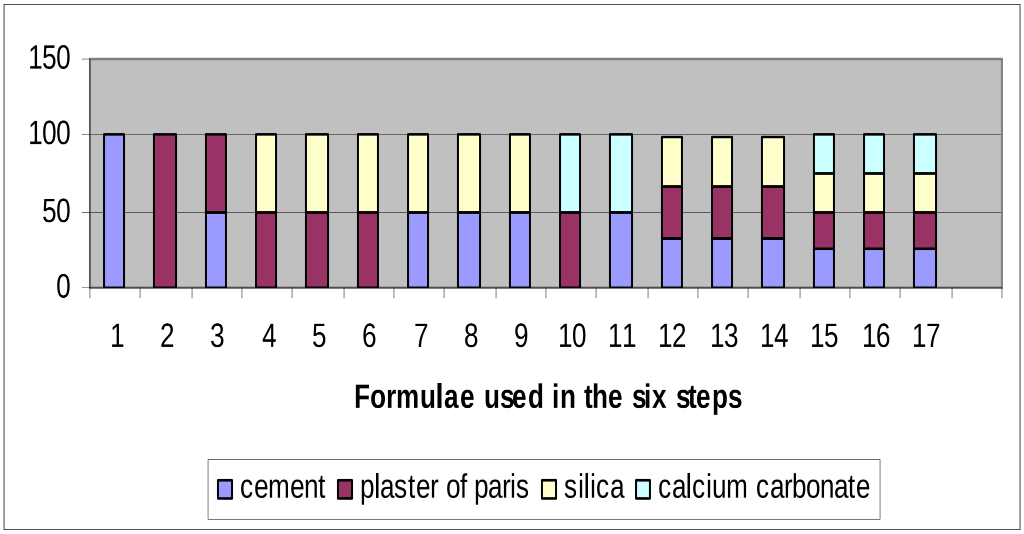
Table 1.3 A table format to record temperature and relative humidity parameters.

The disintegrating characteristics recorded in the table similar to the one above will be to produce a set of bar graphs as a visual aid of the comparative characteristics produced by the various core formulae under investigation.

1.5.15.3 Column graph

An example of a typical column graph designed to illustrate the core formulations juxtaposed with the disintegrating times.

A graph will be designed to illustrate the material composition of each formula juxtaposed with its disintegrating elapsed time. This graph will be arranged as illustrated in table 1.6. (Note the disintegration times are not recorded here as they still have to be determined).



Graph 1.3 The arrangement of the formulae on the graph is set out above is an illustrative example.

1.5.16 The wax test moulds for use in experimental bronze pours

Three different wax moulds will be used to examine selected core formula performance in the bronze casting scenario investigated in the fifth sub-problem.

Firstly, hollow wax tubes 300 mm x 30 mm (approximately 200 ml) will be used to investigate the characteristic effects that will occur when removing the various selected formulae from the long narrow bronze casts. These wax tubes will also be used for multiple testing of sets of formulae combinations, as they will be more practical to use in group testing than single wax casts such as the female torso described below.

Figure 1.13 A photograph of three examples of thirty centimeter high wax tubes that will be used on their own or in sets, to test various parameters of the core formulae in the fifth sub-problem.

Secondly, a hollow wax model in the form of a female torso with a height of 300 mm and an internal volume of one and a half litres will be used to further investigate potential core formulae selected from the hollow tube experiments. In this case the female torso will introduce further variables being of a larger volume than the wax tubes and thus lead to further investigations of the core formulae.

Thirdly, a four-litre hollow wax form in the shape of an open-ended container in the shape of a mask will be used as the upper limits for the investigation into the feasibility of developing a disintegrating core formula that will be suitable for everyday use in the small art bronze foundry (cf. background to the problem).

Figure 1.4 A photograph of the wax female torso that will be used to test various formulae in the fifth sub-problem. Note the core pins are in place.

Figure 1.5 A photograph of a four-litre wax model of a typical mask that will be used for core testing in fifth sub-problem.

1.5.17 The procedure for investing the compound mould discussed above in the ceramic shell material

The ceramic shell mould is built up in layers around the compound wax moulds with the attached pouring cup (cf. Lomax, 2001: 16).

Briefly, the method that will be used to build the ceramic shell mould is explained as follows:

- The outer surface of the wax mould is first painted with shellac and methylated spirit mixture that acts as a bonding agent to the water based silica sol slurry. After the shellac mixture has dried on the wax mould, it is then dipped into the prepared colloidal sol slurry and sprinkled with 0,2 – 0,7 mm chamotte

- After drying for four hours, the mould is again dipped into the colloidal sol slurry and sprinkled with 0,2 – 0,7 mm chamotte,

- This procedure is repeated four more times to produce a ceramic shell coating approximately 5 mm thick,

- The final dip into the colloidal sol slurry is called the seal coat. It is not finished with a sprinkling of chamotte but left with the coating of the last slurry dip,

- The ceramic mould is then allowed to dry for twenty-four hours,

- This process normally takes seven days to complete,

- The mould is now ready for flash de-waxing and the subsequent sintering firing to 945^{0}C with a thirty-minute soak period at 945^{0}C.

1.5.18 Firing the ceramic mould prior to bronze casting

Due to the expansion of microcrystalline wax when it is heated, there is a definite possibility that this expansion could cause the ceramic shell mould to crack with fatal consequences to the subsequent bronze pour.

A standard flash de-wax method has been developed to counteract this expansion of the microcrystalline wax within the ceramic shell mould.

The flash de-wax method is described as follows:

The invested mould is subjected to the heat of a propane flame that rapidly heats the ceramic shell mould. The outer layers of the wax mould inside the ceramic shell melt first and are expelled from the mould before the major portion of the wax inside the mould can expand, thus preventing the cracking of the ceramic mould.

This flash de-wax method can also be performed in a special electric kiln with a bottom vent to allow molten wax to exit the kiln (cf. Lomax 2001: 20).

1.5.18.1 Sintering the ceramic shell containing the test core

Apart from the need for empirical consistency, the ceramic shell mould containing the core has to be sintered to strengthen and harden the invested ceramic shell mould so that it can withstand the sudden rise in temperature to approximately 600^0C when exposed to the de-waxing process and also to the hot molten bronze, which is poured at approximately 1200^0C. This sintering process for the ceramic shell is normally carried out in an electric kiln where the temperature is raised to specific temperatures in the region of 900^0C to 1000^0C depending upon the manufacturer's recommendations for their particular brand of colloidal silica sol (cf. Young and Fennel, 1986: 111).

In this investigation, Levasil 4063 (cf. appendix VIII) is the colloidal silica sol of choice used by the PET bronze foundry and will be used for the ceramic shell investments throughout this study. The temperature of the sintering process will be between 900^0C and 1000^0C depending on the temperature requirements necessary to produce a core that will disintegrate within 48 hours.

1.5.18.2 Firing temperatures for the cores in the bronze casts

The firing temperatures for the core formulations in this investigation will be between 900^0C and 1000^0C with an intermediate temperature at 945^0C with a thirty-minute soak period. The temperatures fall within the sintering temperatures prescribed for the ceramic shell process as indicated in 1.5.18.1 above.

A thirty-minute soak period should allow the temperature to penetrate into the core in the experiments for bronze casting as the heat in the kiln has to cross the air barrier within the mould caused by the loss of the wax mould during the de-waxing process. To read the temperature within the core during the firing process a thermocouple will be inserted into the core so that it reaches at least three quarters way into the core. The temperature of the kiln will be set in a hold or soak mode to enable the temperature inside the core to rise to the temperature recorded in the kiln. This is referred to as the soak period.

Figure 1.16 A photograph of a thermocouple inserted into a core prior to firing. The photograph shows the pyrometer which records the temperature of the thermocouple.

1.5.19 Removing the sintered moulds from the electric kiln

The fired moulds can be removed from the kiln (using suitable leather gloves and a body protection uniform) as soon as the core has reached its designated temperature and the bronze is poured into the mould whilst it is still hot. However, a six hour window of opportunity (in which the sintered core can be held for up to six hours and still be useable in a bronze pour) will be investigated. The core theoretically is expected to begin disintegrating as soon as it reaches its fired temperature of between 900^0C and 1000^0C (cf. spalling in the literature review 1.4.7) so that the mould containing the core should be filled with molten bronze as soon as possible after the core reaches its optimum sintering temperature, but it should have the capacity to be kept for up to six hours after this time to account for any unexpected delay in pouring the molten bronze.

1.5.20 Pouring bronze into the sintered ceramic shell moulds

The hot bronze (when at approximately at 1200^0C) will be poured into the moulds as soon as possible after their removal from the sintering kiln. These two operations must be closely synchronized, as it must be remembered that the cores within the ceramic shell mould theoretically begin to deteriorate as soon as they reach room temperature, the parameters of which will be tested for in sub-problem 1.

1.5.21 Exposing the core to the atmosphere after the bronze pour

After the bronze pour is complete the test moulds will be left to cool to room temperature. At this stage the outer ceramic shell will be broken away from the bronze cast. This procedure will expose the core to the atmosphere at the end opposite the pouring cup.

1.5.21.1 Measuring the disintegration times of the different cores contained within the bronze castings

The test bronze castings obtained from the procedure above containing the different selected core formulae will then be observed for their disintegrating potential.

The time will be noted from when the castings have cooled to room temperature and this will be recorded as the beginning of the time interval, to the time when the core formulae can be easily raked or gouged out of the test bronze castings, which are referred to as the disintegration time.

1.6 DELIMITATIONS

Introduction

The methodology and the hypotheses that will be formulated for this thesis will be limited to the small art bronze foundry as represented by a leading teaching foundry (i.e. the PET sculpture foundry, Port Elizabeth, South Africa).

The bronze cast work produced in this studio foundry is normally for hollow bronze cast statuettes and art works, usually no more than 300 mm high with a capacity of one and a half litres. In this regard, the volume constraints will be limited to no more than one and a half litres experienced in the every-day conditions that occur at the PET art bronze-casting foundry. However, larger volumes are sometimes required to be cast, for example heads with an approximate internal volume of three and a half litres. It is felt that if the envelope on volume is pushed to a top limit of four litres, then this will suffice the top requirements of a small art bronze foundry.

Further, sophisticated methods, instruments and apparatuses outside the scope of the small art bronze foundry will be avoided and rather simulations close to those that can be found or innovated in the small art bronze studio will be used so that the processes conducted throughout this investigation can be repeated and used within this scenario.

The research approach will have a clear correspondence to what is more typically termed “action research”. Here, “action research” is understood to be a flexible spiral process which allows action (change, improvement) and research (understanding, knowledge) to be achieved at the same time. The understanding allows more informed change and at the same time is informed by the change.

1.6.1 Chemical and physical reactions. A full understanding of the chemistry and physical reactions that occur in the compounded formulae mixes made throughout the development of a disintegrating core will be addressed as reasonably as possible, but it is not expected that details or analysis of these occurrences and reactions be recorded herein.

1.6.2 Firing temperatures for the naked test bars will be to 900^{0}C, 945^{0}C and 1000^{0}C respectively (cf. literature review 1.4.3 where the sintering temperatures are discussed by Young and Fennel, 111).

The naked test bars will initially be used to investigate different combinations of the five ingredients (cement, calcium carbonate, plaster of paris various grades of silica and calcium hydroxide) to determine their response to the above three temperatures which lie within the sintering temperatures of the ceramic shell investment moulds.

1.6.3 Firing temperatures for the core formulae will be finalized between 900^{0}C and 1000^{0}C when used in the bronze casting process and will include a soak period of approximately thirty minutes at the top temperature to allow the kiln temperature enough time to penetrate the interiors of the cores within the ceramic shell mould.

1.6.4 Disintegration times. The core that will be developed for use in the ceramic shell process must disintegrate within 48 hours.

In consultation with Mr. D. Jones, resident art sculpture lecturer at the PET, it was considered that in the light of the difficulties experienced in removing core material from hollow bronze casts at present, that it would be advantageous if a core could be developed that could be easily removed within 48 hours from its bronze cast.

This disintegrating time limit was set as the maximum practical elapsed time that would be allowed for a core to disintegrate so that it could subsequently be quickly and easily removed from the hollow bronze cast.

1.6.5 Curing time for a core under investigation will be for seven days, which also falls within the general time frame for the ceramic shell mould construction times observed as a common practice at the PET art bronze foundry (cf. literature review 1.4.7).

According to Kellerman, cement cures to a maximum strength within twenty-eight days but it also reaches a moderate degree of strength within seven days (cf. Fulton’s concrete technology, 2001: 214 – 215). However, the 28-day strength is used in concrete strength specifications but under favourable conditions concrete can gain strength for years. As the formula to be developed will contain a certain amount of cement and the general time taken to invest a mould with the ceramic shell is deemed to take seven days, seven days will be the taken as the minimum curing time required beginning from the time of pouring the core into the mould to sintering the core within the mould to prepare it for the bronze pour.

1.6.6 Water will be de-ionized water procured from a well maintained calibrated water de-ionizing plant.

De-ionized water will be used throughout the investigation as a wetting agent to make the different test formulae into pourable masses. De-ionized water will serve as a standard for this investigation.

1.6.7 Formula test pieces for the experiments in the first four sub-problems will be made in the form of rectangular bars, with dimensions of 100 mm x 20 mm x 20 mm in a silicone rubber mould specially constructed for this purpose (cf. figure 1.5) The test pieces will be referred to as naked test bars in the text.

The naked test bar format will be used as a means to quickly test the disintegrating characteristic outcomes of different formulae combinations, as opposed to the long process of testing experimental formulae in the bronze casting process.

At advanced stages of formulae testing it may be necessary to test core formulae in larger volume formats to determine any characteristic changes that may occur between the naked test bars (40 ml) and larger naked brick shaped bars 200 mm x 100 mm x 50 mm or 1000 ml.

1.6.8 All measurements will be by parts per volume. All measurements will be by parts per volume in this investigation into the development of a disintegrating core and the final formula will be converted to mass measurements in order that future investigators will have an additional point of reference to work from.

1.6.9 Empirical testing in sub-problems 1- 5. The experiments that will be conducted to address the sub-problems will be of an exploratory nature and will be conducted in such a manner that the sequential results derived from these tests will be to indicate in which direction the core formulations being investigated should be further developed.

A minimum of three tests will be performed for each exploratory experimental test to verify the results obtained in these tests. However, where the results cannot be supported by testing evidence, the testing procedure will be suspended at that point in the investigation.

1.6.10 Shrinkage values should be equal to or less than 1% in the final formula. Six different readings from six different naked test bar pieces having the same formula will be recorded prior to firing of the naked test bars and also immediately after the kiln has cooled to room temperature. The naked test bars will be the format for all shrinkage evaluation tests (cf. methodology 1.5.).

The limits namely 1% or less, where determined to be within art studio foundry tolerances, as discussed with D. Jones, sculptor lecturer at the PET in consultation with G. Detleefs, owner of Ingwe Editions, Koelenhof 7605 South Africa, manufactures and fabricators of fine bronze castings.

1.6.11 Compressive strengths The compression values (using the Hounsfield testing apparatus) will be taken to indicate comparative compressive strengths between different fired core formulae.

These compressive strengths will be used to indicate how the formulating of core bodies can be adjusted by either increasing or decreasing certain ingredients in a formula. For example, a fired formula with x % of silica may have an increase in strength if the silica value is reduced, which may at the same time decrease the shrinkage value and in turn increase the disintegrating time of the core formula.

1.6.12 Relative humidity tests will be conducted at different humidity readings to determine the effect of humidity on the disintegrating times of the sintered core formula. Three humidity values will be chosen for testing purposes, being a high relative humidity (91%), a moderate relative humidity (approximately 81%) and a low relative humidity (approximately 73%). These values have been chosen as representative of the values previously recorded in Port Elizabeth during March to November 2003, inside the R H C apparatus in the room set aside, away from draughts and direct sunlight (cf**.** methodology 1.5.13).

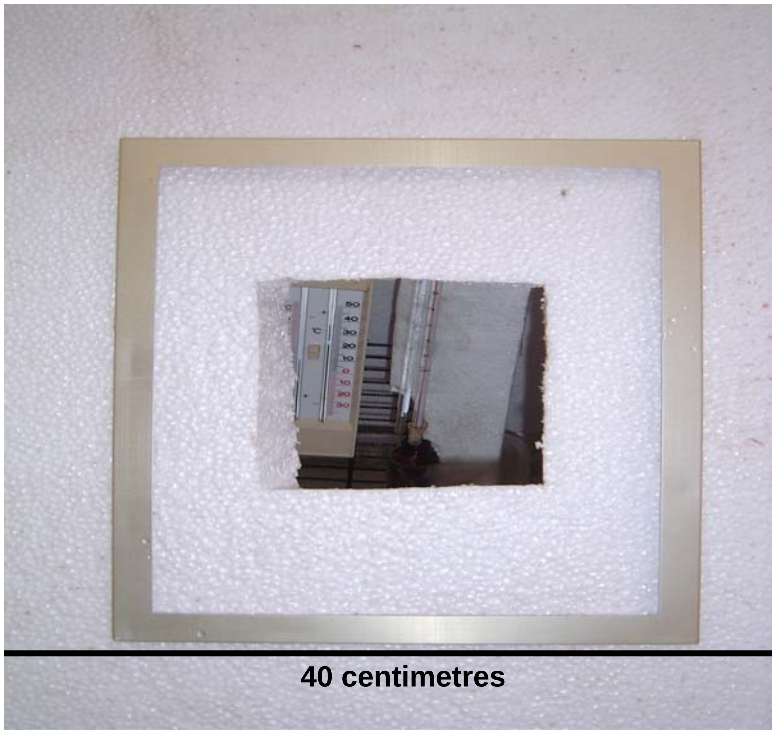


Figure 1.17 A photograph illustrating a view through the lid of the R H C apparatus.

1.6.13 Volume limits for moulds used with cores in an art bronze scenario. Three different wax test models will be made in the form of hollow tubes (300 mm x 30 mm with a volume of approximately 100 ml), thirty-one centimeter tall wax female torsos (volume approximately 1500 ml) and a four litre, open-ended container (sometimes with a face added to represent a mask), will be used to investigate formulae in bronze casting scenarios conducted in sub-problem 5.

1.6.14 The materials selected for the formulae tests will be limited to the following ingredients:

1.6.14.1 Silica: 0,074 mm, purchased from the LaFarge Ready Mix in Port Elizabeth (cf. product specifications in appendix II). Silica 0,2 mm graded size purchased from Consolidated Ltd, Cape Town (cf. product specification in appendix III). Silica 0,95 mm silica from B and E (Pty) Ltd, Delmas (cf. product specifications appendix IV).

Different particle sizes of silica were chosen to be used in the formula experiments to determine whether a powder (0,074 mm) an intermediate size (0,2 mm) or a larger size of 0,95 mm would impose different effects upon the characteristics of the sintered formula being investigated. These three silica particle sizes were chosen as they are freely available from most hardware and swimming pool suppliers.

1.6.14.2 Cement: (Pretoria Portland Cement) brand Surebuild code CEM 11 / A-L 32.5 Portland limestone cement, SABS ENV 197; Parameters 80-94% clinker with 6-20% limestone (cf. literature review 1.4.7 and appendix I).

This particular type of cement was chosen as it is the cement manufactured in Port Elizabeth and is thus locally available. In consultation with the chemist at PPC (Pretoria Portland Cement), Mr Hermanus Potgieter, the fact was stated that cements with different additives, for example fly ash, would possess different properties and could not simply be related one to the other. For this reason and for keeping the number of ingredients to the minimum in the development of a disintegrating core formula it was decided to work only with this one type of cement produced in Port Elizabeth (cf. appendix I).

1.6.14.3 Calcium carbonate, trade name: Kulubrite-10

Calcium carbonate in the form of a fine powder was selected as in this fine state the conversion time to CaO would be shorter than for a coarser material in the firing process. If larger particles of calcium carbonate were selected i.e. Kulubrite 40 only partial calcinations could occur, due to the fact that in the ceramic shell process, the top sintering temperature is held for only a brief period of time as occurs in the practical application of the bronze pouring process (cf. product specifications in appendix V).

1.6.14.4 Calcium hydroxide, trade name Limbux Hydrated lime

Calcium hydroxide was chosen as an alternative to calcium carbonate to verify whether it would be superior or inferior in its contribution to the disintegration of core formulae (cf. product specification in appendix VI).

1.6.14.5 Plaster of paris, Manufactured by BPB Gypsum (Pty) Ltd. Technical Services, Cape Town (cf. product specification in appendix VII).

1.7 ASSUMPTIONS OF RESEARCH

1.7.1 Technical data

It will be assumed that all technical data as supplied by the manufactures is accurate as stated in their product literature (cf. appendices).

1.7.2 Instrumentation

It will be assumed that all instrumentation is accurate. For example, the temperature readings recorded by the electric temperature recorders attached to the sintering kilns will be verified using Orton pyrometric cones. Two relative humidity apparatuses will be used alongside one another to verify the readings. The results obtained using the Hounsfield compression instrument are computer generated and this machine is regularly calibrated by the engineering department at the PET.

1.8 RATIONALE

Core bodies usually made and used in small bronze studio foundries where the ceramic shell process is employed, are difficult to remove from the cast bronze piece due to their hard refractory properties.

A simple method of core removal would be an advantage to these studios, as a great deal of time is spent in non-productive work removing cores from bronze art pieces.

A refractory formula acting as a core, that can be easily poured into a hollow wax model, which will then break up due to its inherent disintegrating properties after the bronze pour, would be a welcome addition to general foundry procedures.

With the knowledge of a desired core formula that will disintegrate after a bronze pour, the bronze practitioner would be able to produce cast pieces that do not have to be cut into smaller pieces to remove unwanted core material.

1.9 HYPOTHESES

Introduction

A core body that is poured into a hollow wax model for use in the lost wax bronze casting method should be easily removed from the cast bronze, yet be strong enough to be held by holding pins within the ceramic shell mould during the bronze casting process and should also have a minimum shrinkage value, so as not to alter the parameters of the bronze that will replace the wax that has been melted out of the ceramic shell mould.

1.9.1 First hypothesis

With the manipulation of certain materials or a combination of materials, one will initially be able to produce a quick-setting naked core formula that will disintegrate within 72 hours under controlled conditions of temperature and relative humidity.

1.9.2 Second hypothesis

An effective formula, which is developed in the first hypothesis, will disintegrate with further formulae manipulation within a specific period of time, namely 48 hours, and will have a shrinkage value of equal to or less than 1%.

1.9.3 Third hypothesis

The relative humidity will have an influence on the disintegration times of the fired naked core bodies.

1.9.4 Fourth hypothesis

The temperature to which the naked core body is heated during the ceramic shell sintering process will have a significant influence on the disintegration and strength of the formulated core body.

1.9.5 Fifth hypothesis

Once the four sub-problems have been addressed above, a disintegrating core formula can be developed that will be easily removed from the hollow bronze cast, leaving minimal residue that can be speedily removed by using either or both a gouging metal tool or a sandblasting machine.

1.10 DEFINITION OF TERMS

1.10.1 Bronze casting activities:

These are activities that are normally concerned with the bronze casting process. For example they will include wax mould production, core formulations, ceramic investment procedures as well as the pouring of molten bronze into the sintered ceramic moulds.

1.10.2 Disintegration of the core and core removal from the cast bronze:

Disintegration of a core formula or core body in the context of this thesis shall deem to mean a core formulae, which when exposed to the atmosphere after firing to between 900^0C and 1000^0C with a thirty-minute soak period (i.e. the temperature is held at the upper temperature limit for thirty minutes before the electric kiln is switched off), will break down to a powdery mass after a prescribed period of time. In the case where the core is within a cast-bronze piece, disintegration will deem to mean the stage when the core can be easily gouged out of the hollow bronze and /or removed using a sandblasting machine set at 6 bars pressure and using a shot approximating 0,2 – 0,7 mm chamotte (grog), without difficulty. The term is used here in the normal context of a small foundry where previous cores using the PET formula do take many long hours, involving tedious mechanical processes (cf. background to the problem using the PET core formula page 1-10). The disintegration of the core will be formulated to specifically disintegrate within 48 hours from the time the core has been fired to between 900^0C and 1000^0C and subsequently been removed from the sintering kiln. The bronze should be poured into the hollow mould containing the core within six hours of switching off the sintering kiln otherwise the disintegration process may progress too far and the core may become too weak to support a bronze pour.

1.10.3 Naked test bar:

This term describes a core formula when made into test bars in a silicone rubber mould (cf. methodology 1.5.8). These naked test bars will be used to evaluate sub-problems 1 to 4. They are tested “naked” as opposed to the core formulae which are evaluated within hollow bronze casts conducted in experiments in sub-problem 5. The naked test bar format is used as a means to quickly test the disintegrating characteristic outcome of different formula combinations, as opposed to the long process of testing experimental test formulae enclosed within bronze casts.

1.10.4 Pourable mass, including the setting time and curing time of the freshly made core material:

The time taken for the pourable formula mix to set into a weak but firm mass, usually occurs within 10 minutes after adding the requisite amount of de-ionised water to the mix, and becomes a firm mass after 6 hours (cf. glossary quick-setting formula). At this stage, a wax mould containing the core mass can be invested using the ceramic shell process. The quantity of de-ionized water that is added to the formula to achieve a pourable mass (cf. volumes in table 6.2) is important for three reasons namely:

- If the quantity of water exceeds the values obtained by experimentation (cf. table 6.2) the already wet mixture suddenly becomes very runny and it serves no purpose as this water has to be expelled again from the core during the de-wax process;

- The smaller the volume of water, within certain parameters, that is added to the mixture containing cement, the stronger the mix will be (cf. Fulton' s concrete technology 2001:7, B. Addis);

- The smaller the volume of water, within certain parameters, that is added to the formula containing plaster of paris, the stronger the mix will be (cf. literature review, table1.2).

As the factors mentioned above can all produce variable results, it is important that the volume of de-ionized water as well as the quantities of the other ingredients in the mix is observed to ensure repeatable results can be obtained for the formula mixes.

1.10.5 Spalling The term spalling used in this document refers to the `negative nature of concrete when exposed to elevated temperatures (cf. Connolly *et al.*1996: 43). Connolly *et al.* further states that spalling is due to pore pressure in concrete and it may be minimized if the amount of free moisture within the concrete is reduced, either artificially or through aging.

However, in the formulations that will be conducted in the development of a disintegrating core, cement will be diluted by the addition of materials such as calcium carbonate powder and plaster of paris in powder form. This dilution of the cement will probably reduce the spalling effect referred to by Connolly *et al.* (1996: 43).

1.10.6 R H C apparatus (relative humidity control apparatus)

The effect of water in the form of water vapour in the atmosphere on calcium oxide in experimental test cores after being heated to 900^{0}C and above converts calcium oxide to calcium hydroxide, with an expansion in volume, which could be disruptive in the test core formulae. Calcium oxide is formed in the test formulae from the calcium carbonate or calcium hydroxide as well as that formed in the hydration of cement (cf. literature review: 1.4.7 Cement and 1.4.10 calcium carbonate).

Different degrees of humidity will be considered when evaluating the effect that different concentrations of water vapour have on the disintegration of the sintered core mixes. The ambient temperatures in Port Elizabeth can vary in one day from a high of 31^{0}C to a low of 5^{0}C with a relative humidity variant of 100% in foggy weather to 50% on a dry day (cf. information obtained in consultation from the South African Weather Services at the Port Elizabeth airport).

Description of the R H C apparatus (relative humidity control apparatus) and the methods for its use

- A secluded room has already been selected as a workstation where the R H C apparatus would be kept throughout this investigation in order to conduct the relative humidity tests.

- These general relative humidity conditions are important as they will be an indication as to how a high, moderate and lower relative humidity would affect the disintegrating times of the sintered formulae, which would be in the form of naked test bars to be covered in chapters 4 and chapter 5.

Figure 1.18 A photograph illustrating a view through the lid of the R H C apparatus. showing a maximum and minimum thermometer (relative humidity) as well as the wet and dry thermometers which are calibrated in half degree centigrade divisions.

Figure 1.19 A photograph of a view looking down into the R H C apparatus which for illustration purposes has six sintered test bars placed on a metal grid above a trough of water

1.10.7 Wide range of hollow bronze casts

A wide range of hollow bronze cast volumes will be investigated using different wax models to determine the suitability of the disintegrating core within these moulds.

These hollow wax models will be:

- A long narrow wax tube 300 mm x 30 mm with a volume of 200 ml.
- A female torso 300 mm tall with a volume of 1500 ml.
- An open-ended mould in the form of a mask 240 mm high with a volume of 4000 ml.

1.11 OVERVIEW

The following, is a brief overview of the layout of the thesis, chapter by chapter:

CHAPTER 1

Chapter 1 will be the introduction to the research, what the study is about and the reasons for the study. This will include the background to the problem, statement of the research problem, the sub problems, the literature review, the methodology, the delimitations, the rationale, the hypotheses and the definition of terms.

CHAPTER 2

Here the first sub-problem will be restated:

What materials or combination of materials can be used to produce a quick-setting core formula for use in the ceramic shell process that will disintegrate within 72 hours, under controlled conditions of temperature and relative humidity?

A record of the studies of the relationship between four different materials that were chosen for this thesis will be studied alone and in combination.

Seventeen experiments will be conducted in sub-problem one. Test bars 100 mm x 20 mm x 20 mm made from the various formulae for these tests, will be used in experiments to evaluate the formulations under review.

This chapter will conclude with a summary of the findings of the first sub-problem.

CHAPTER 3

Here the second sub-problem will be restated:

What is the most effective formula that can be developed from the most promising formulae investigated in the first sub-problem, which will ensure that the core-body with quick-setting characteristics will disintegrate within 48 hours after firing and still have a shrinkage value of equal to or less than 1%?

A record of the studies of the relationships between disintegrating time and shrinkage values will be undertaken.

Ten formulations will be used to investigate sub-problem two. Test bars made from the formulae under review will once again be used to ascertain the characteristics of these formulae pertaining to shrinkage and disintegrating times.

This chapter will conclude with a summary of the findings for the second sub-problem.

CHAPTER 4

Here the third sub-problem will be restated.

What are the relative humidity considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal studio bronze casting procedures?

This chapter will record the outcome of the studies undertaken to show to what degree relative humidity affects disintegrating times of three selected formulae from sub-problem two.

The three formulae will be subjected to four different relative humidity conditions to ascertain the relationship between disintegration of the formulae and relative humidity.

Test bars 100 mm x 20 mm x 20 mm will once again be used in these experiments.

The chapter will conclude with a summary of the findings for the third sub-problem.

CHAPTER 5

Here the fourth sub-problem will be restated:

What are the temperature considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal ceramic shell sintering parameters?

Once the four sub-problems have been addressed, the resultant formula/formulae will be examined in bronze cast field tests, as opposed to the exploratory naked core tests already conducted to examine whether the detected parameters affecting the sintered core temperatures, relative humidity, and elapsed time as well as the formula/ formulae compositional parameters will be valid in this instance?

This chapter will record the outcome of the relationship studied between the temperature considerations and the constraints of ceramic shell sintering parameters.

Two selected test formulae from sub-problem three will be subjected to three different sintering temperatures and the disintegrating factors will be ascertained against two different relative humidity environments.

The chapter will conclude with a summary of the findings relevant to the fourth sub-problem.

CHAPTER 6

Here the fifth sub-problem will be restated:

Would the conclusions inferred in the first four sub-problems be applicable to core formula/formulae when used for the actual production of a wide range of hollow bronze casts?

This chapter will record the outcome of the tests conducted in an actual bronze pour tests using a selected core formulae in the ceramic shell process and will also review the parameters for a core with disintegrating properties.

Seven experiments will be conducted in this chapter to re-examine the effects of relative humidity, sintering temperatures and core formulation in the bronze casting scenario. The chapter will conclude with a summary of the findings relevant to the fifth sub-problem.

CHAPTER 7

Chapter 7 is the conclusion. Here all pertinent data and analysis will be critically reviewed in the light of the problem of the research and its five sub-problems. In addition, all methodologies will be reviewed as to their efficacy and possible improvements to the methodology will be discussed. Lastly, further research suggested by the project will be indicated.

CHAPTER 2

EXPERIMENTAL PROCEDURES: SUB-PROBLEM 1

The experiments under review in this chapter were undertaken with a view to solve the following sub-problem.

What materials or combination of materials can be used to produce a quick-setting core formula for use in the ceramic shell process that will disintegrate within 72 hours, under controlled conditions of temperature and relative humidity?

2.1 Foreword

The experiments under review for this chapter will be limited to a probing investigation, comprising of six pilot experiments in which cement, plaster of paris, silica and calcium carbonate (calcium hydroxide will be experimented with in chapter 3) will be moulded into test bars and referred to hereafter as naked test bars (cf. def. of terms 1.10.3), will be examined alone and in various combinations to determine their individual or combined characteristics when heated to 945^{0}C and kept in a R H C apparatus in a room set aside for relative humidity testing purposes. (cf. def. of terms 1.10.6).

The materials that were chosen for experimental purposes (cf. literature review 1.4) to evaluate the question asked in sub-problem one were thoroughly tested in a series of incremental steps mentioned above, to determine to what degree they could play a role in a disintegrating core body. The ambient temperature and related humidity were taken at the prevailing room temperature and relative humidity at the time of these introductory tests, as no set limits for these parameters had been established at this time. The initial time limit for disintegration was set at sixty hours and extended to 72 hours to understand and to establish what was happening to the core formulae (especially the formulae containing cement) that had been sintered to 945^{0}C (cf. literature review 1.4.3). The temperature of 945^{0}C was chosen as the intermediate experimental temperature between 900^0C and 1000^0C to provisionally understand what was happening at this temperature to various core formulae under investigation.

2.2 Review of the incremental steps that led to the pathway for the disintegrating core investigation (cf. methodology 1.5.4).

The first step

The first step in the investigation is to determine the physical spalling properties of pure cement. In addition it will also be necessary to determine the effects on plaster of paris or a mixture of cement and plaster of paris that has been fired to 945^0C. (Spalling in cement has been discussed in the literature review 1.4.7).

The second step

The second step in the process is to determine the effect on plaster of paris when mixed with silica 0,074 mm, silica 0,2 mm and silica 0,95 mm and fired to 945^0C.

The third step

The third step is to determine the effect on pure cement when mixed with silica 0,074 mm, silica 0,2 mm and silica 0,95 mm and fired to 945^0C.

The fourth step

The fourth step is to determine whether powdered calcium carbonate will affect the fired characteristics of either cement or plaster of paris when heated to 945^0C.

The fifth step

The fifth step is to determine the combined effect of plaster of paris and cement with either silica 0,074 mm, silica 0,2 mm or silica 0,95 mm when fired to 945^0C.

The sixth step

The sixth step is to determine the characteristics of an equal mixture of plaster of paris, cement, calcium carbonate and either silica 0,074 mm, silica 0,2mm or silica 0,95mm when fired to 945^{0}C.

The seventh step

The seventh step is to evaluate the parameters obtained in the six steps above and to formulate further pathways that could lead to the determination of a successful disintegrating core.

2.3 Review of the materials to be tested in the experimental formulae

The different raw materials that will be used in these series of incremental steps are listed below (cf. methodology 1.5.7):

- Cement will be used for its binding and spalling contribution.

- Plaster of paris will be added to the various formulae to determine its binding and quick setting properties as a contribution to the various formulations.

- Silica will be added in three different particle sizes, to determine the effects in the formulae.

- Calcium carbonate will be added to the experimental core formulae as a possible disintegrating material due to its conversion to calcium oxide at high temperatures and re-conversion to calcium hydroxide upon cooling.

- De-ionized water will be used to make pastes with all the various formulae having sufficient fluidity to flow into the test silicone moulds.

2.4 A review of the formulae to be tested in steps one to six

The formulae are made up in parts per volume.

The first step	
Formula F1	
Plaster of paris	100%
Formula F2	
Cement	100%
Formula F3	
Plaster of paris	50%
Cement	50%
The second step	
Formula F4	
Plaster of paris	50%
Silica 0,074 mm	50%
Formula F5	
Plaster of paris	50%
Silica 0,2 mm	50%
Formula F6	
Plaster of paris	50%
Silica 0,95 mm	50%

The third step	
Formula F7	
Cement	50%
Silica 0,074 mm	50%
Formula F8	
Cement	50%
Silica 0,2 mm	50%
Formula F9	
Cement	50%
Silica 0,95 mm	50%
The fourth step	
Formula F10	
Plaster of paris	50%
Calcium carbonate	50%
Formula 11	
Cement	50%
Calcium carbonate	50%

The fifth step	
Formula F12	
Plaster of paris	33,3%
Cement	33,3%
Silica 0,074 mm	33,3%
Formula F13	
Plaster of paris	33,3%
Cement	33,3%
Silica 0,2 mm	33,3%
Formula F14	
Plaster of paris	33,3%
Cement	33,3%
Silica 0,95 mm	33,3%
The sixth step	
Formula F15	
Plaster of paris	25%
Cement	25%
Silica 0,074 mm	25%
Calcium carbonate	25%
Formula F16	
Plaster of paris	25%
Cement	25%
Silica 0,2 mm	25%
Calcium carbonate	25%
Formula F17	
Plaster of paris	25%
Cement	25%
Silica 0,95 mm	25%
Calcium carbonate	25%

2.5 Introduction to the testing procedure

The tests conducted for the purpose of addressing sub-problem 1, were conducted between March and November 2004, when the ambient temperature and the relative humidity varied between 14^0C and 24^0C and the relative humidity between 64% and 73% in the room set away from draughts and direct sunlight.

In this regard, the above mentioned formulae were all mixed and individually poured into the test silicone mould to form the test bars (cf. methodology 1.5.9.3). The naked test bars were then kept in the R H C apparatus in the designated control-room for seven days to cure (cf. glossary), away from draughts and direct sunlight that could affect the drying parameters of the test bars.

The naked test bars from each formula were then fired to 945^0C (Orton cone 08, cf. glossary) and subsequently removed from the kiln when the kiln once again reached room temperature. The bars were then placed in the sequential order of the six steps on the metal grid (cf. figure 1.12), in the R H C apparatus in the designated control-room. The naked test bars were then observed for any disintegrating characteristics from time when the bars had reached room temperature after being fired to 945^0C and then at six hourly intervals as recorded in the figure 2.1 below.

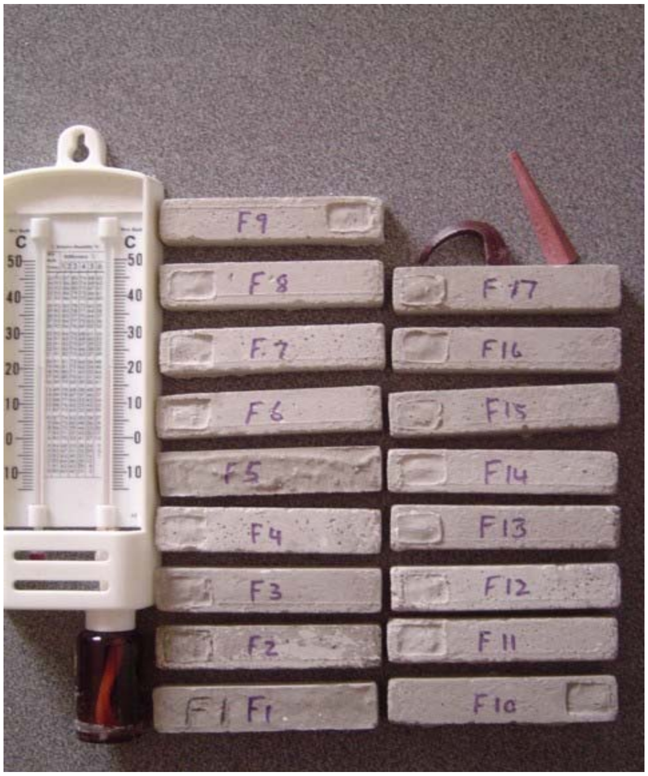


Figure 2.1 A photograph illustrating the seventeen naked test bars fired to 945^0C that have just been removed from the kiln.

The Orton cone indicates that the temperature of the kiln reached 945^0C. As yet, the test pieces have not visibly begun to disintegrate. The first visual indication that disintegration of the test pieces is occurring is when cracks on the surfaces of the naked test bars begin to appear.

Results and discussion

The following figures 2.2 to 2.6 illustrate a series of photographs in which pure cement (F2) and a combination of cement and calcium carbonate (F11) show the different characteristics of the spalling phenomena for these two naked test bars. This series of photographs illustrates the idea that by adding extra calcium carbonate to cement different degrees of disintegration (spalling) will occur to that of pure cement. The test was carried out in the R H C apparatus at between 16^0C and 19^0C with a relative humidity at between 64% and 73%.

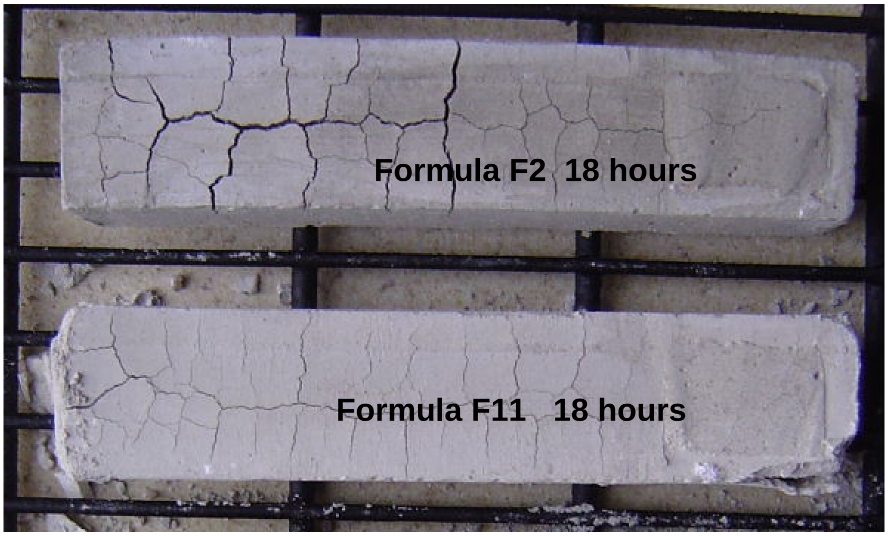


Figure 2.2 The photograph illustrating the cracks that appear on the surfaces of both naked test bars 18 hours after having been removed from the kiln fired to 945^{0}C. The naked test bar on top is pure cement and the bottom test bar, F11 was made from an equal proportion of cement and calcium carbonate.

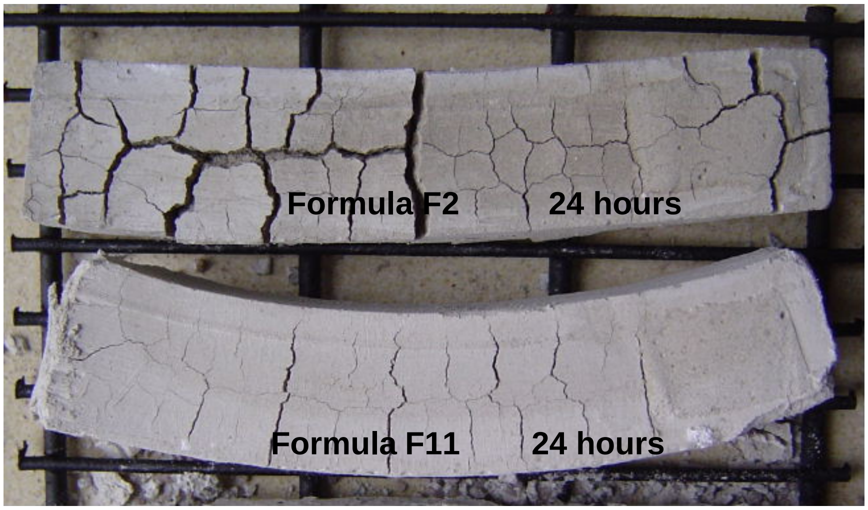


Figure 2.3 A photograph illustrating the breaking up of formula F2 and F11 after 24 hours.

Formula F2, which is composed of pure cement is spalling in an expected fashion, as explained in the literature review 1.4.7. Formula 11, which is composed of equal parts by volume of cement and calcium carbonate, appears to be reacting more slowing to disintegration forces of its constituent ingredients. Naked test bar F11 is also warping to one side which occurred whenever the experiment was repeated.

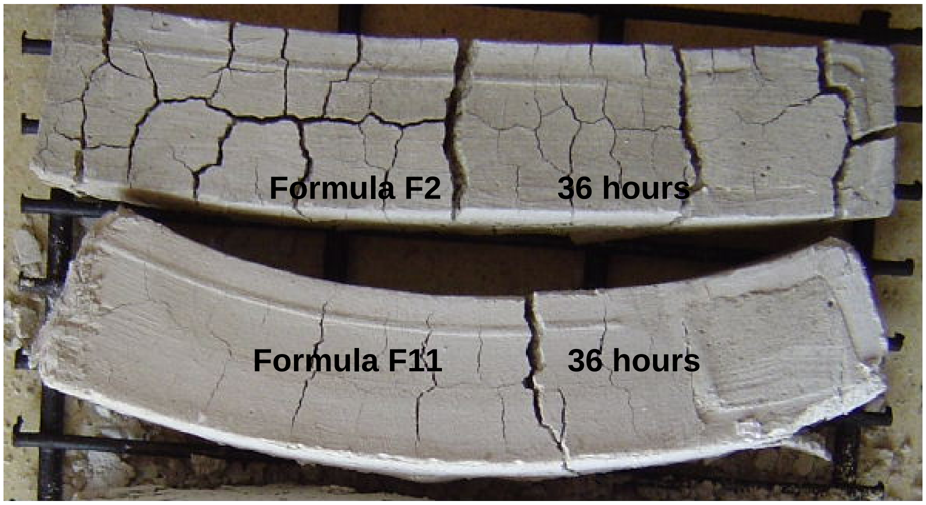


Figure 2.4 A photograph of the two naked test bars F2 and F11 after 36 hours. F11 has warped even closer towards F2 and larger cracks to the right of F2 have appeared as it continues to break up at a faster rate than F11.

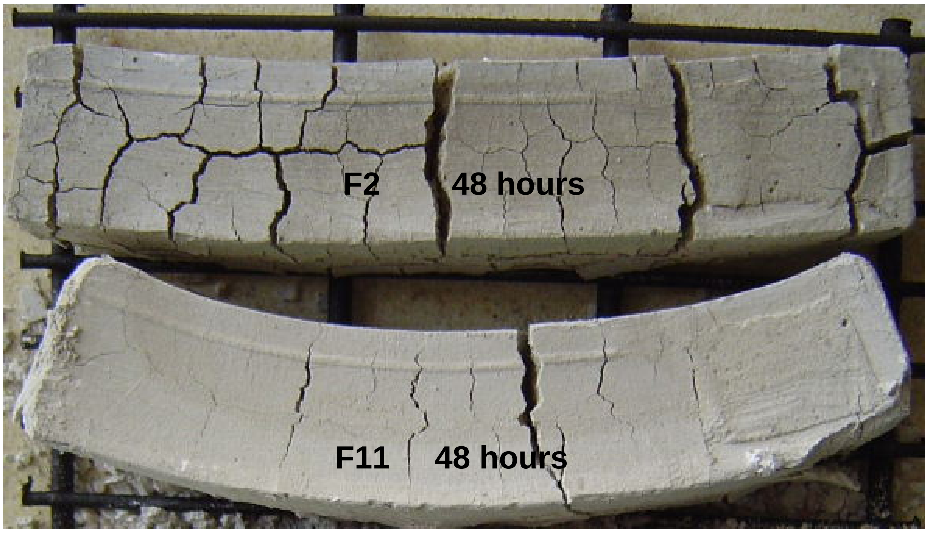


Figure 2.5 A photograph of F2 and F11 after 48 hours.

The warping effect seen in formula F11, which consists of an equal proportion of cement and calcium carbonate, may be due to the physical nature of the mass disintegrating after having been fired to 945^{0}C. This combination of materials made in the form of naked test bars and fired to 945^{0}C, warped to one side in every instance. However when silica was added to the formula in F12, F13 and F14 the naked test bars did not warp after being fired to above 945^{0}C.

Figure 2.6 Formula F2 (pure cement) broken into large soft powdery chunks when lightly touched after 72 hours.

Figure 2.7 Formula 11 also broke into large soft powdery chunks when lightly touched after 72 hours.

The addition of calcium carbonate to cement in formula F11 produced a more unified body which disintegrated very similarly to pure cement but without the large cracks. The contribution of the combined ingredients still had too great a shrinkage percentage (2,3% cf. table 2.1) which would subsequently be reduced by the addition of silica. The setting time after pouring the wet mix into the silicone rubber mould was also too long (12 hours) and plaster of paris would be required to improve this problem in later formulations.

2.6 Observations

	Elapsed time	Begin	24 hours	36 hours	48 hours	60 hours	After 72 hours
	Ambient temperature	16-19^{0}C	16- 19^{0}C	16-19^{0}C	16-19^{0}C	16-19^{0}C	16-19^{0}C
	Relative humidity	64-73%	64-73%	64-73%	64-73%	64-73%	64-73%
Formula	Setting time	Average % Shrinkage	Disin-tegration	Disin-tegration	Disin-tegration	Disin-tegration	Disin-tegration
F1	1 hour	9,9%	nil	nil	hard	hard	hard
F2	12 hours	2-3%	surface cracks	surface cracks	breaks into soft chunks (spalling)	Remains in soft chunks	Remains in soft chunks
F3	5 minutes	6,2%	large hard cracks	hard cracks	hard cracks	hard cracks	hard cracks
F4	4 hours	1.6%	hard	hard	hard	hard	hard
F5	4 hours	1,9%	hard	hard	hard	hard	hard
F6	4 hours	2.3%	hard	hard	hard	hard	hard
F7	12 hours	1.3%	hard	hard	hard	hard	hard
F8	12 hours	1,3%	hard	hard	hard	hard	hard
F9	12 hours	1,4%	hard	hard	hard	hard	Can be gouged out
F10	12 hours	10,8%	hard	hard	hard	hard	Can be gouged out
F11	12 hours	2,3%	cracks	cracks	chunks	chunks	Powdery chunks
F12	6 hours	1,4%	hard	hard	hard	Can be gouged out	Can be gouged out
F13	6 hours	1,4%	hard	hard	Can be gouged out	Can be gouged out	Can be gouged out
F14	6 hours	2,1%	hard	hard	Can be gouged out, but hard	Can be gouged out	Can be gouged out
F15	6 hours	1,5%	hard	hard	hard	Can be gouged out	Can be gouged out
F16	6 hours	1,6-1,7%	hard	Surface cracks	Beginning to break down	Beginning to break down	Breaks down in 72 hours
F17	6 hours	1,7%	hard	Surface cracks	Beginning to break down	Breaks down within 60 hours	powdery

Table 2.1 A table setting out the results of the experiments conducted in steps one to seventeen.

The results recorded above would be used as indicators in the search for further parameters that could eventually lead the investigation in producing a workable disintegrating core formula. The relationships between formulae, for instance where different grades of silica are added in parts per volume to make up different formulae, for example F4, F5 and F6, cannot be scientifically correlated to each other as the variables introduced by this measuring system are too numerous to make accurate assumptions. However, the volume measuring system does give an indication of the trends that are occurring, which then allows for the deduction of further formulations, which is the intention of this research.

2.7 The seventh step

The results of the seventeen tests conducted in the six steps are discussed below to illustrate the characteristics of each test.

- Formula1, made from pure plaster of paris, remained a hard mass after 72 hours with a high shrinkage value of 9,9%. The inclusion of the plaster of paris into the formulae was for its value as a binding and setting agent;

- Formula 2, made from pure cement produced a dense mass that exhibited spalling characteristics, by breaking up into small soft chunks that remained in this condition past the 72 hour limit set in sub-problem 1. However, the chunks when probed with a sharp metal point, showed that their contents were quite powdery and with gentle prodding using the sharp metal point, the chunks could be easily broken up.

The combination of cement and plaster of paris in formula F3, had a shrinkage value of 6,2%. The mix set rapidly within five minutes of adding water compared with one hour for the plaster of paris and twelve hours for the cement. This indicates that plaster of paris will prove to be beneficial in a cement mix to achieve a quick-setting formula. However the shrinkage value is high and the formula will require further manipulations to achieve values below 1%. The formula remained as hard broken chunks to the 72 hour time limit (cf. table 2.1).

Below are photographs illustrating the spalling effect when cement and plaster of paris are combined in equal proportions and fired to 945^{0}C and then kept in a R H C apparatus at between 64% and 73%.

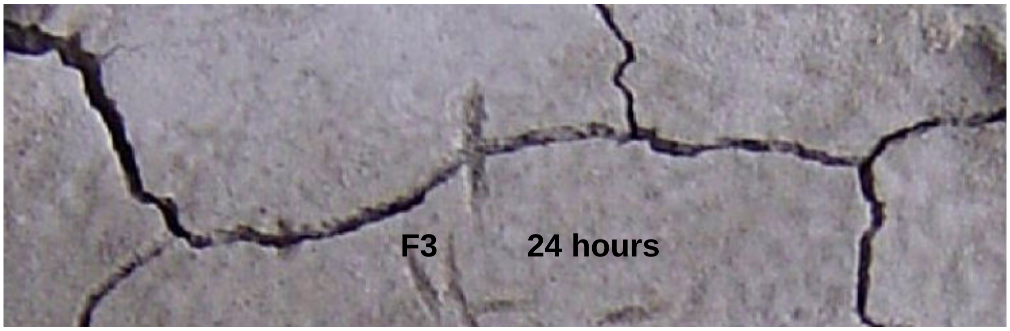


Figure 2.8 Details of the cracks that appeared on the surface of Formula F3, 24 hours after being fired to 945^{0}C. The formula set into a hard mass within 5 minutes of pouring into the silicone rubber (cf. table 2.1).

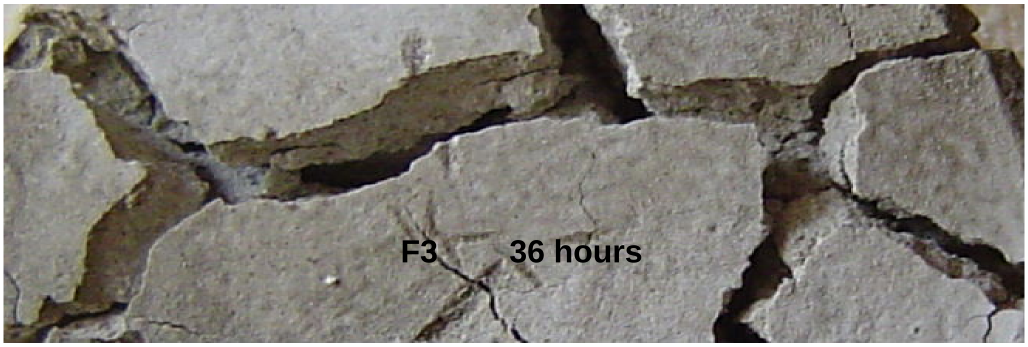


Figure 2.9 Formula F3 after 36 hours. The cracks have increased dramatically but the cracked sections remain as hard chunks (cf. table 2.1).

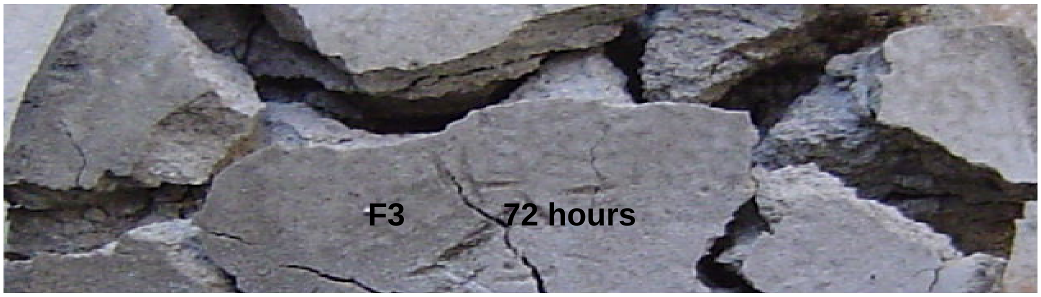


Figure 2.10 Formula F3, the combination of cement and plaster of paris remained as broken hard chunks after 72 hours.

- In the second step, formulae F4, F5 and F6, produced hard masses, which did not soften to any degree after 72 hours. The addition of different grades of silica to the plaster of paris in these formulae reduced the shrinkage of pure plaster of paris dramatically to between to between 1,6% and 2,3%.

- In the third step, the combined contribution of cement and silica produced a hard mass with a low shrinkage values between 1,3% and 1,4% but they did not exhibit any of the spalling characteristics that were found in formula F2. The silica particles apparently prevented the cement from spalling in these formulae. Silica, however was retained for future formulations due to its contribution of reducing the shrinkage rate in the formulae, that is, pure cement had a shrinkage rate of between 2% and 3% and when mixed with silica (cf. formula F9) the shrinkage was reduced to 1,4%.

- The fourth step introduced the combination of plaster of paris with calcium carbonate or cement with calcium carbonate. The plaster of paris combination (F10) gave a shrinkage value of 10,8%, and still remained hard after 48 hours. In the case of the cement and calcium carbonate combination (cf. formula F11) the mass had broken into chunks with a powdery nature within 72 hours. The shrinkage value was fairly low at 2,3%, but still above the desired value of 1%.

The following series of photographs illustrates the behaviour of a plaster of paris and calcium carbonate mixture, formula F10 after being fired to 945^0C and kept in a R H C apparatus at between 16^{0}C and 19^{0}C with a relative humidity at between 64% and 73%.

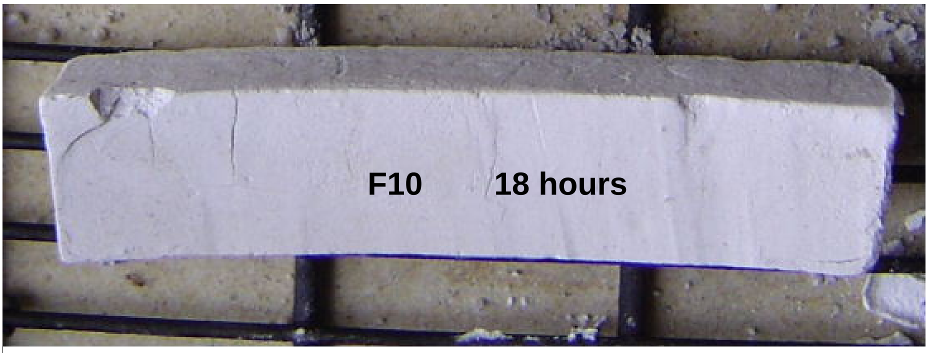


Figure 2.11 A photograph of the fired naked test bar F10 made from equal parts by volume of plaster of paris and calcium carbonate after 18 hours (cf. table 2.1).

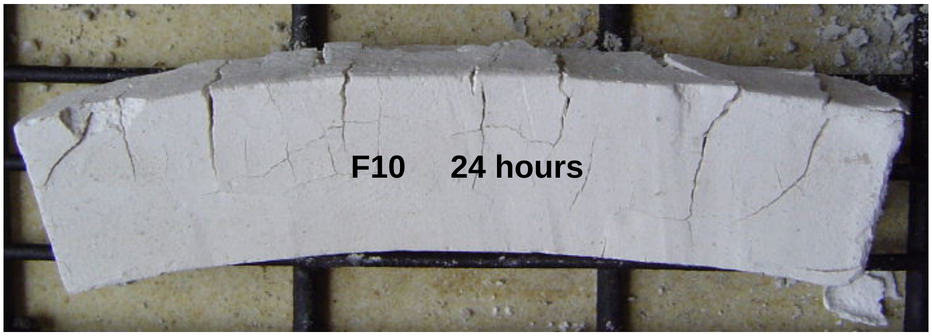


Figure 2.12 A photograph of F10 warping in shape after 24 hours as more dominant cracks develop (cf. table 2.1).

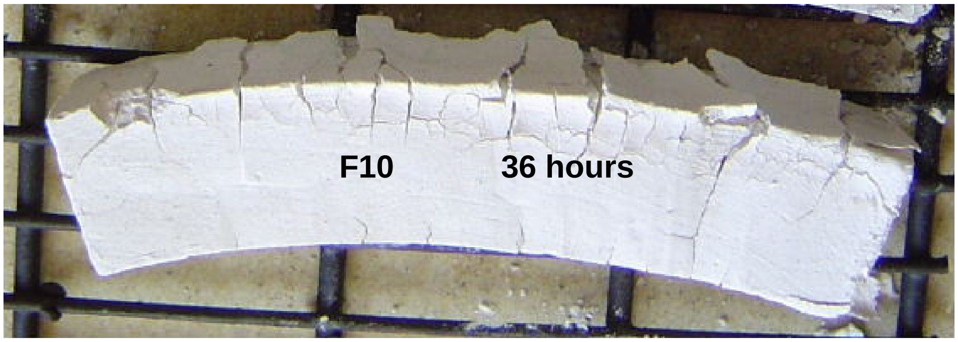


Figure 2.13 A photograph of F10 after 36 hours.

The plaster of paris and calcium carbonate combination produced exfoliated surface sheets as illustrated in the photograph.

This characteristic exfoliation occurred in repeated tests conducted under similar conditions of temperature and relative humidity.

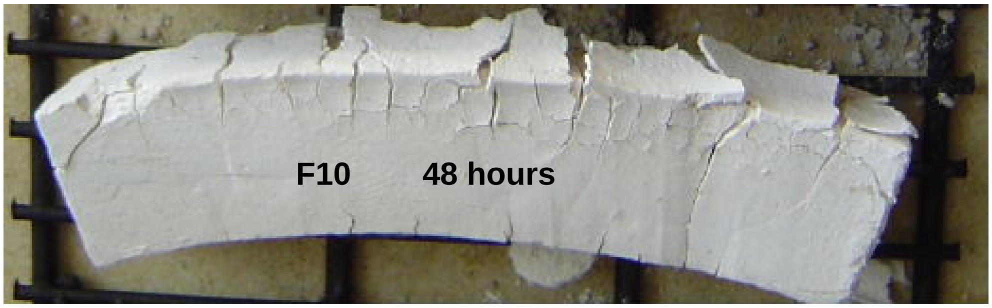


Figure 2.14 The photograph illustrating that the exfoliation process is continuing at a slow rate.

This exfoliation effect appears on the side where cracks first appear, which indicates that calcium oxide formed when calcium carbonate was fired to 945^{0}C is slowly converting to calcium hydroxide at a relative humidity of between 64% and 73%.

Figure 2.15 Formula F10 remains firm and soft after 72 hours and has not disintegrated into a powder.

- The fifth step included formulations composed of a combination of plaster of paris, cement and different particle sizes of silica. These formulae produced masses that remained fairly hard. The shrinkage values were all low, being 1,4% for each of formulae F12 and F13 and 2,1% for formula F14.

- The sixth and final step in this series produced two formulae, F16 and F17, that began to break down within 48 hours and after 60 hours both these two formulae could be easily powdered by crushing between the fingers with the minimum of finger pressure. Formula F15, containing the very fine silica 0,074 mm, remained firm beyond 48 hours and only after 60 hours had the surface become soft enough so that it could be gouged out using the point of a metal probe.

- The shrinkage values of formulae F15, F16 and F17 were between 1,5% and 1,7%. Although formula F15 had the lowest shrinkage value, it was not chosen as a prospective formula for further development, as the silica 0,074 mm appeared to be the ingredient that retarded the disintegration of the formulae. Both silica 0,2 mm and silica 0,95 mm when included in similar formulae, produced masses that both began to break down within 48 hours, with F17 showing the most promise as regards disintegrating properties, although it had a similar shrinkage rate as F16.

2.8 The review that follows, illustrates a further pathway that led to the formulation of more successful experimental core formulae.

The characteristics of the four ingredients under review, namely, plaster of paris, cement, silica and calcium carbonate will be discussed for their contribution to a disintegrating formulation. As already indicated in table 2.1, the four ingredients were fired in different combinations with each other to 945^0C and after cooling to room temperature were kept at between 16^0C and 19^0C with a relative humidity between 64% and 73% for 72 hours in the R H C apparatus.

2.9 A discussion of the formulae fired to 945^0C

- Pure plaster of paris had a 9,9% shrinkage value and remained hard after 72 hours. This material appears to have no real value as a contributing agent to a disintegrating core formula. However, plaster of paris does have a binding and a rapid-setting action, which are the two criteria, required for a successful disintegrating core formula.

- The addition of silica to plaster of paris in the second step indicated that silica 0,074 mm produced the formula having the lowest shrinkage value, whilst silica 0,95 mm had the highest shrinkage value. This factor in this instance only indicates that the addition of silica to plaster of paris reduces the shrinkage value. The addition of silica 0,2 mm to plaster of paris (cf. formula F5), produced a mass that remained hard after 72 hours, but the shrinkage value had been reduced to 1,9%. The addition of silica 0.95 mm produced similar results, with a shrinkage value slighter higher at 2.3% (cf. formula F6).

- The combination of plaster of paris and calcium carbonate (F10) produced a firm mass, which remained in this state even after 72 hours with an unsatisfactory shrinkage value of 10,8% (cf. figure 2.15). This formula combination should have been discarded, but the combination of cement and calcium carbonate (F11) produced a product that began to break down into chunks within 48 hours and became powdery within 72 hours (cf. figure 2.7). However, pure cement also produced a product that had spalling characteristics by breaking up into chunks (cf. figure 2.6), within 72hours.

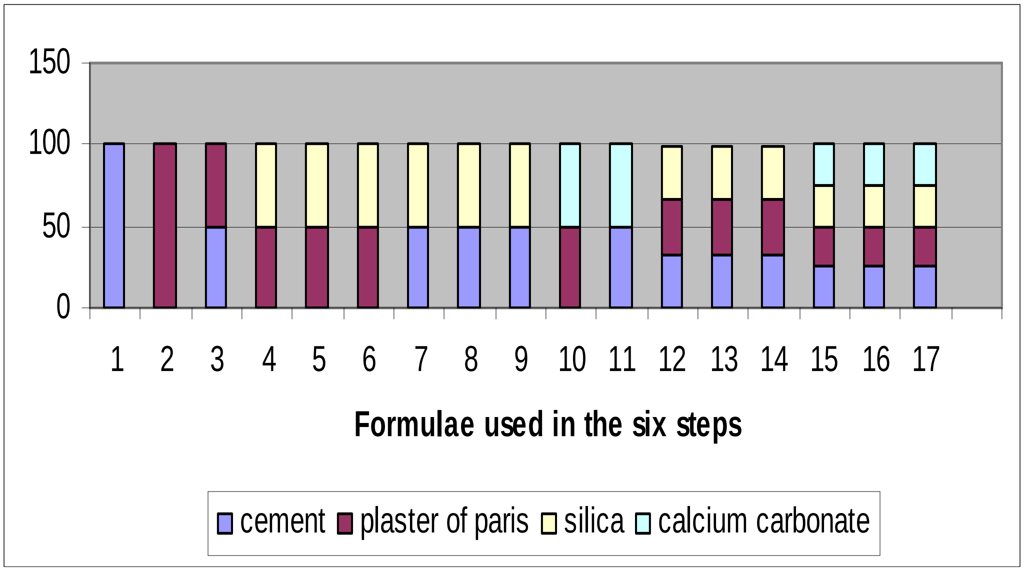
- A formula that showed early promise was the combination of cement and calcium carbonate (cf. formula F11) which had a relatively low shrinkage rate of 2,3%, which began to crack within 48 hours and became powdery within 72 hours.

- Formula F13 having a composition of plaster of paris, cement and silica 0,2 mm in equal parts, produced a mass with a shrinkage value of 1,4% and had a surface that that could be easily gouged out within 48 hours with the aid of a sharp metal probe. After 60 hours, the mass had become softer than before.

- The inclusion of calcium carbonate in equal proportions with the other components, for example, plaster of paris, cement and silica 0,2 mm (F16) or 0,95 mm silica (F17), produced satisfactory results in the formulae F16 and F17. Both these formulae began to break down within 48 hours and both had shrinkage values between 1,6% and 1,7%. After 60 hours, both of these formulae could be easily powdered between the fingers with gentle finger pressure. However, F17 appeared to be the formula that broke down more easily than F16 did, although they both had very similar physical characteristics.

Formula F15, which included silica 0,074 mm, remained firm and did not crumble even after 72 hours.

Table 2.2 illustrates the seventeen formulae and the disintegrating relationships between the four test materials when mixed in various proportions to form the preliminary core formulations, fired to 945^{0}C and observed at between16^{0}C and 19^{0}C and at a relative humidity of between 64% and 73%.



Graph 2.1indicating the various material combinations and their relationships to one another.

The combination of materials in F16 and F17 produced the most promising preliminary disintegrating naked test bar results. All the other combinations of materials alone or in combination did not produce the same overall results that F16 and F17 did by breaking into a powdery mass within 60 and 70 hours respectively and with low shrinkage values of between 1,6% and 1,7%.

2.10 Further experimentation

Formulae F16 and F17 produced the best disintegrating results, in that they slowly started to break down within 72 hours with a soft powdery composition. However, both these formulae also displayed fairly high shrinkage values of between 1,6% and 1,7%, which were above the 1% being sought (cf. methodology 1.5.11 as an upper limit for a core-body. In chapter 3, formulae F16 and F17 would be further modified to determine whether by altering the formulations they could be made to disintegrate within 48 hours and simultaneously have their shrinkage rates reduced to below 1%.

CHAPTER 3

EXPERIMENTAL PROCEDURES: SUB-PROBLEM 2

The experiments under review in this chapter were undertaken with a view to solve the following sub-problem

What is the most effective formula that can be developed from the most promising formulae investigated in the first sub-problem, which will ensure that the core-body with quick-setting characteristics will disintegrate within 48 hours after firing and still have a shrinkage value of equal to or less than 1%?

3.1 Foreword

The experiments undertaken for this chapter concentrated on formulae F16 and F17 as well as modifying them to produce further formulae that would disintegrate within 48 hours, yet display a shrinkage value of 1% or less. A comparison was also made between the inclusion of either calcium carbonate or calcium hydroxide in these formulae.

In chapter two, it was noted that the two sintered naked test bars (cf. formulae F16 and F17) displayed promising disintegrating characteristics by beginning to show surface cracks after 48 hours but did not completely disintegrate within 48 hours. Unfortunately these two formulae were found to be handicapped by having high shrinkage values.

The pathway that achieved a reduction in the disintegrating time as well as having achieved a shrinkage value of below 1% was achieved by reducing either the cement or the plaster of paris in different steps in the following formulae, namely formulae F19 to F22, whilst adjusting the silica and the calcium carbonate values accordingly.

The following table 3.1, details the disintegrating characteristics obtained by having fired the naked test bars under investigation to 945^{0}C and then having kept the test pieces at an ambient temperature that varied between 16^0C and19^0C at a relative humidity of between 64% and 73%% in the R H C apparatus.

Formulae	**F 16**	**F 17**	**F 18**	**F 19**	**F 20**	**F 21**	**F 22**
Cement	1	1	3	2	1	2	1
Plaster of paris	1	1	2	2	2	1	1
Silica 0,95mm	1 Silica 0,2 mm	1	1	1	2	2	3
Calcium carbonate	1	1	1	2	2	2	2
Disintegration	70 hours	60 hours	60 hours	60 hours	70 hours	55 hours	48 hours
Shrinkage	1,6% to 1,7%	1,7%	1,8%	2,1%	1,5%	1,0%	0,9%
Firing temperature	945^0C	945^0C	945^0C	945^0C	945^0C	945^0C	945^0C
Relative humidity	Varied between 64–73%	Varied between 64–73%	Varied between 64–73%	Varied between 64–73%	Varied between 64–73%	Varied between 64–73%	Varied between 64–73%
Ambient temperature	Varied between 16-19^0C	Varied between 16-19^0C	Varied between 16-19^0C	Varied between 16-19^0C	Varied between 16-19^0C	Varied between 16-19^0C	Varied between 16-19^0C

Table 3.1 Recorded values obtained for formulae F16 – F22

3.2 A photographic record illustrates the sequence of events that took place in the disintegration of a fired naked test bar using formula F21 as the example

Six naked test bars with the formula F21 fired to 945^0C were kept in a R H C apparatus at between 16^0C and 19^0C at a relative humidity of between 64% and 73%. One of the test bars was photographed at time intervals of 20 hours, 30 hours, 40 hours and 55 hours to indicate the break down of the test bar and so define the time when the naked test bar would be regarded as having disintegrated.

Results and discussion

3.3 Photographic disintegration measurements

The photographic disintegration measurement recorded below, although not exactly the same in every instance, was used as a general indication of when all future fired naked test bars (which included the four ingredients of cement, calcium carbonate, plaster of paris and silica) could be regarded as having disintegrated (cf. methodology 1.5.15.1 and 2).

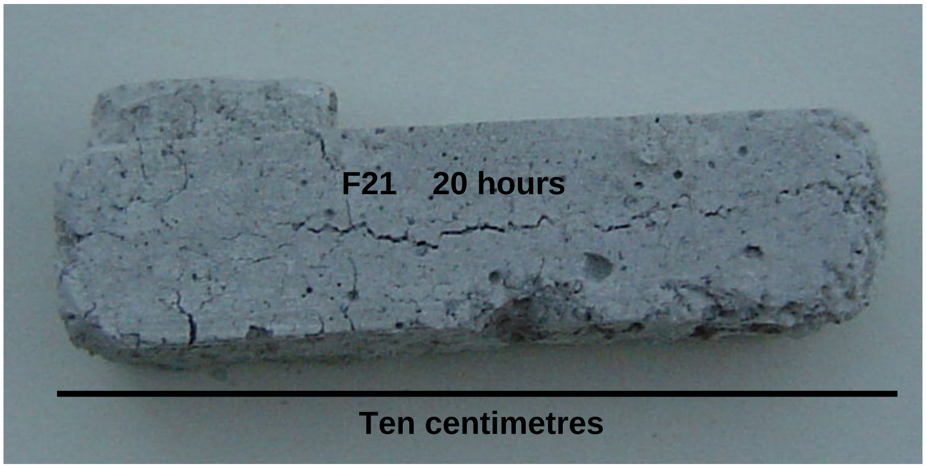


Figure 3.1 The naked test bar (F21) with surface cracks appearing after 20 hours.

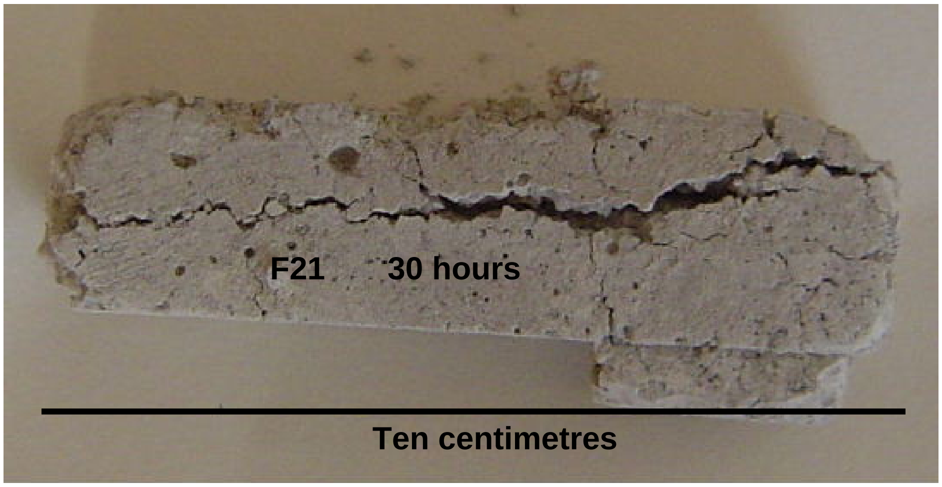


Figure 3.2 The naked test bar (F21) with enlarged surface cracks opening after 30 hours.

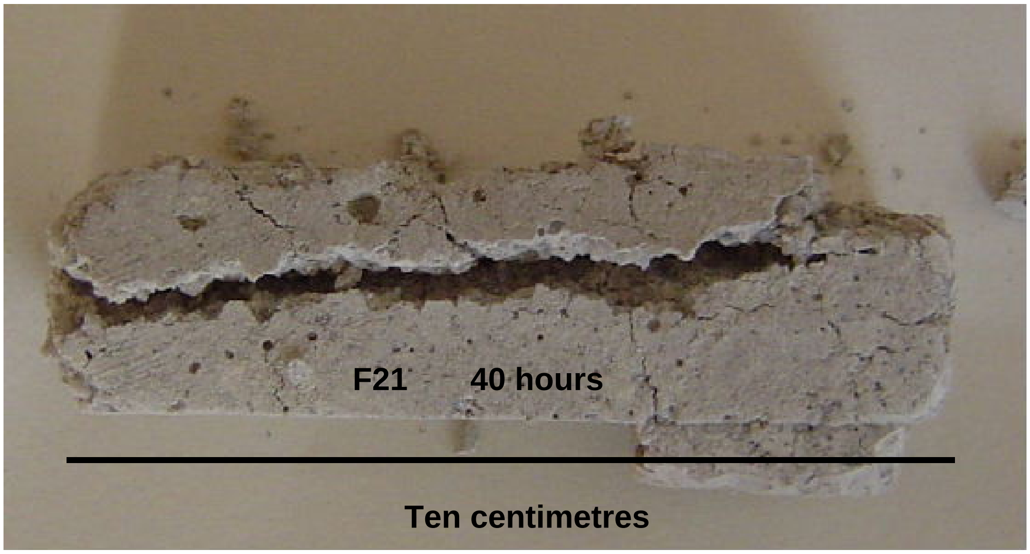


Figure 3.3 The photograph of (F21) illustrates that the test bar has practically fallen apart after 40 hours.

Figure 3.4 The sides of the naked test bar (F21) have fallen away from the main body after 55 hours.

If the mass at this stage is lightly touched, the mass simple crumbles into a heap of powder which includes the unchanged silica particles. The stage at which the test bar falls apart is used as a guide in all fired naked test bar evaluations to indicate when the naked test bar has disintegrated.

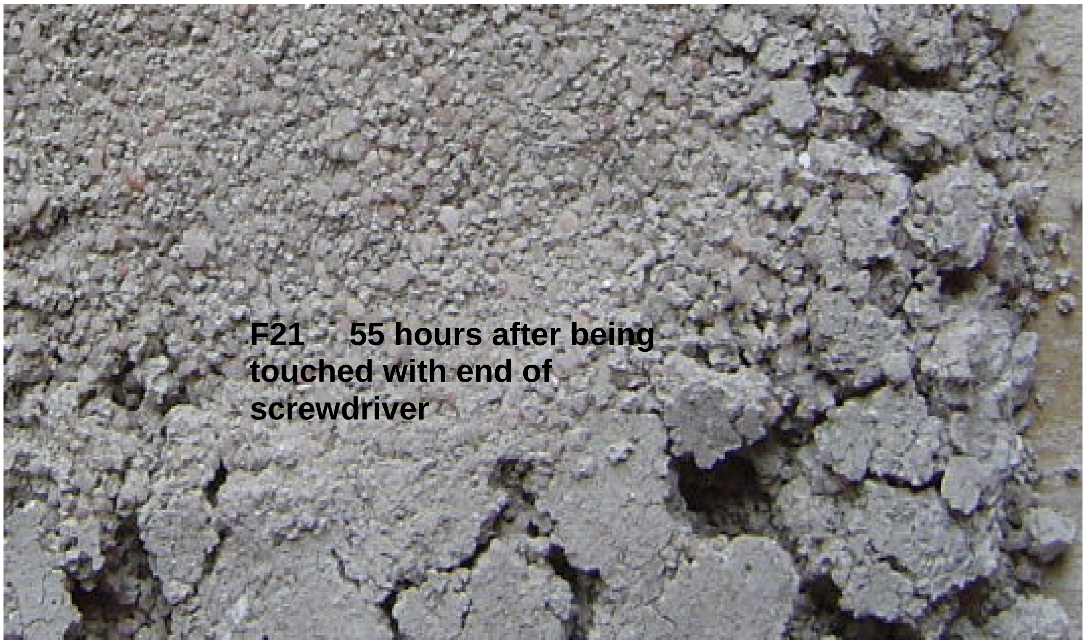


Figure 3.5 A photograph of the disintegrated test bar (F21 in figure 3.4).

The test bar has crumbled into a mass of silica particles interspersed with the powder consisting of cement, plaster of paris and calcium carbonate.

The following microscopic photograph (cf. figure 3.6) illustrates that the disintegrated formula is no longer the unified mass that had originally formed when the materials were mixed with water and allowed to cure for seven days.

The silica particles can be freed from the rest of the disintegrated mass (as can be seen in the photograph as a white powder), by simply dusting away the disintegrated powders using a small soft brush.

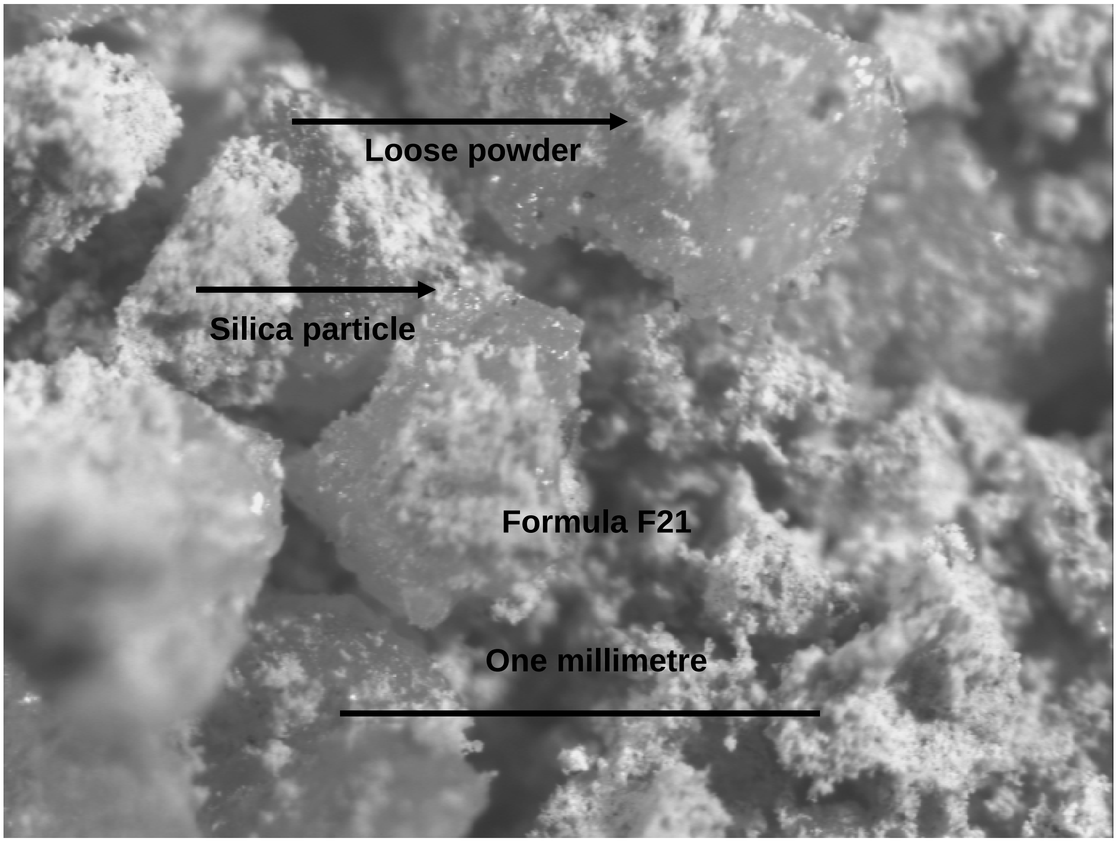


Figure 3.6 A microscopic photograph of the disintegrated formula F21 as recorded after 55 hours (cf. table 3.1). An arrow indicates the loose powder lying on top of the fired 0,95 mm silica particles.

3.3 Observations (with reference to table 3.1)

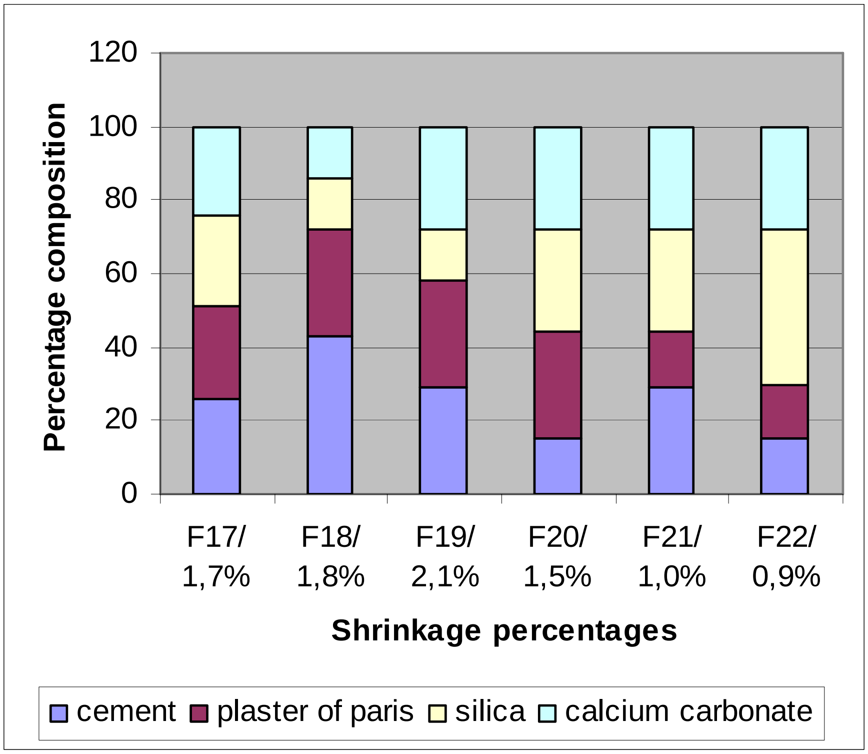
The disintegrating characteristics of formulae F16 to F22 (cf. table 3.1) illustrated the interaction of the four ingredients, (namely cement, plaster of paris, calcium carbonate and silica) in these formulations. Note that F16 is the exception to this series in that it was made using silica 0,2 mm whilst the remainder of the formulae were compounded using 0,95 mm silica. The formula containing 0,2 mm silica was included here to illustrate that the smaller particles of silica delayed the disintegrating process when compared to silica 0.95 mm (cf. table 3.1 the comparison between formulae F16 and F17).

Formula F16 when compared with F17 had a longer disintegrating period, being in the order of 70 hours versus 60 hours for F17. it should be recalled that in chapter 2, sub-problem 1, table 2.1 that the smaller silica particles delayed the period of disintegration, and this phenomenon was also borne out in F15, where a similar formula was used but silica 200 mesh was used instead of silica 0,2 mm. In formula F15, the formula did not disintegrate even after 70 hours had elapsed, thus indicating the positive attributes of using silica 0,95 mm in the development of a disintegrating core.

In formulae F18, F19 and F20, the disintegrating times were similar although different formulae combinations were used (cf. table 3.1). The disintegrating values all proved to be greater than the disintegrating time being sought of 48 hours.

The comparison between formulae F20 and F21 (where the quantity of calcium carbonate and silica 0,95 mm were the same in both formulae, but differed from each other in that formula F20 had twice as much plaster of paris as cement, and formula F21 had twice as much cement as plaster of paris showed considerable differences in the disintegrating characteristics. Formula F20 had a shrinkage value of 1,5% where the plaster of paris was twice the content of cement, as compared to formula F21 which had a shrinkage value of 1,0%. The disintegrating characteristic in formula F21, with a cement ratio of twice that of the plaster of paris, produced a disintegrating time within 55 hours, whereas the disintegrating time in formula F20 was 70 hours.

The following graph (cf. table 3.2) illustrates the relationship between the various materials in formulae F17 to F22.



Graph 3.1 A graph illustrating the various shrinkage percentages of formulae F17 to F22 as well as indicating the percentage composition in each formula.

Formula F22 was acknowledged to be the best formula in this series, with a low disintegrating time and a low shrinkage value as compared with the other formulae in this series. For this reason, formula F22 would be further investigated to determine whether by increasing the silica content and keeping the other ingredients proportionally constant, a better disintegrating and shrinkage result could be obtained (cf. disintegration times in table 3.1).

The two formulae with the best results in this series were formulae F21 and F22 with disintegrating times of 55 hours and 48 hours respectively, both having shrinkage values below 1% were chosen for further comparative considerations in chapter 4.

3.4 Further investigative pathways

A further series of experiments was conducted to determine the disintegrating and shrinkage effects that could occur when the silica (0,95 mm) content was increased, using F22 as the base formula.

The relationships between the formulae with increased values of silica 0,95 mm in formulae were conducted in two further experiments being F23 and F24. These three formulae F22, F23 and F24 were compared to determine whether the silica increases would reduce the disintegrating times as well as the shrinkage values.

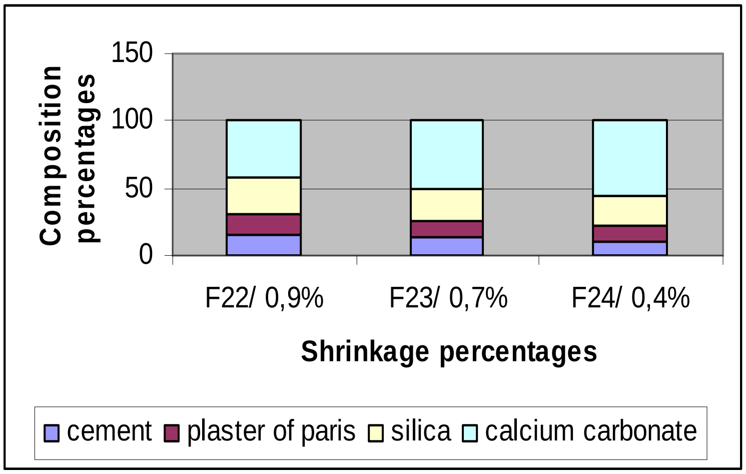
Formula	F 22	F 23	F 24
Cement	1	1	1
Plaster of paris	1	1	1
Calcium carbonate	2	2	2
Silica 0,95 mm	3	4	5
Firing temperature	945^0C	945^0C	945^0C
Disintegrating time	Within 48 hours	Within 48 hours	Within 48 hours
Shrinkage	0,9%	0,7%	0,4%
Ambient temperature	$16\text{-}19^0$C	$16\text{-}19^0$C	$16\text{-}19^0$C
Relative humidity	64-73%	64-73%	64-73%

Table 3.2 A comparative table illustrating the disintegrating and shrinkage values between formulae F22, F23 and F24 where the silica content was incrementally increased in each successive formula.

3.5 Observations

The relationships between the three formulae, namely formulae F22, F23 and F24 were that they all contained the same proportional amounts of cement plaster of paris and calcium carbonate. However, as the silica (0,95 mm) content was incrementally increased from 3 parts in formula F22, to 4 parts in formula F23 and finally to 5 parts in formula F24, so a reduction in shrinkage values occurred (cf. table 3.3). Although formula F24 showed the lowest shrinkage value of only 0,4% after being fired to 945^{0}C, the naked test bar was very weak and tended to break up when handled soon after being removed from the sintering kiln. Formula F22, with a higher shrinkage value of 0,9%, displayed a more robust nature than either F24 or F23. As can be noted in table 3.3, formula F24 has 5 parts of silica whereas formula F22 only has 3 parts of silica and it appeared that as the silica content was increased (the other materials remaining proportionally constant) so the formulae become increasingly weaker with the reduction in shrinkage values.

It must be noted here that the downside to achieving lower shrinkage values in this experiment was that formulae F23 and F24 were very weak when being removed from the sintering kiln and this factor put their usefulness as disintegrating core bodies in doubt. The reader is also reminded here that the cement content in these three formulae constitutes one part of the formula whereas, for example in formula F21 where cement constitutes two parts of the formula.



Graph 3.2 A graph illustrating the composition percentages of the four ingredients in the formulae and the corresponding shrinkage percentages.

The low shrinkage value in formula F24 is superior to F22. However, the downside to this fact is that the formulae were judged to become increasingly weaker to handle as the silica content was increased above the values contained in formula F22.

Formula F22 appeared to be the best compromise at this stage of formulae development in that it produced a core body that disintegrated within 48 hours and had a shrinkage value of less than 1,0%. Formula F22 was therefore selected for the next experiment to compare the effects of calcium carbonate with calcium hydroxide using similar formulae to determine whether calcium hydroxide would be a better ingredient to use in a disintegrating core formula than calcium carbonate (cf. literature review 1.4.5)

3.6 Calcium Hydroxide

In the literature review (cf. 1.4.10) calcium hydroxide was investigated as a possible substitute for calcium carbonate in formulating a disintegrating core-body. The introduction of calcium hydroxide into a formula similar to F22 that will replace calcium carbonate, will be experimented with to determine whether calcium hydroxide is perhaps superior to calcium carbonate in producing a core formula with good disintegrating characteristics, a low shrinkage value and greater strength after being fired to 945^0C.

The comparison between formula F22 containing calcium carbonate and F25 containing calcium hydroxide as ingredients in the formulae is illustrated in table 3.6 below:

Formulae	F22	F25
Cement	1	1
Plaster of paris	1	1
Calcium carbonate	2	_
Calcium hydroxide	_	2
Silica 0,95 mm	3	3
Firing temperature	945^0C	945^0C
Disintegrating time	Within 48 hours	Within 48 hours
Shrinkage	0,9%	0,6%
Ambient temperature	21^0C-23^0C	21^0C-23^0C
Relative humidity	73%-83%	73%-83%

Table 3.3 A comparison between two formulae, one containing calcium carbonate (F22) and one containing calcium hydroxide (F25).

The photograph below (figure 3.7) illustrates how a sharp instrument was used to break up two sintered naked test bars F22 on the left and F25 on the right.

Figure 3.7 A photograph illustrating two partial disintegrated naked test bars made from formulae F22 and F25.

The sharp metal point illustrated in figure 3.7 was used to determine the ease with which it could penetrate the test pieces under investigation. The fired naked test bar F22 is on the left and was more easily penetrated and broken down than formula F25 which contained calcium hydroxide in the place of calcium carbonate.

3.7 Observations

It was assumed that formula F25, which was similar to F22 in ingredient composition (except for that the calcium carbonate was replaced with calcium hydroxide), would possibly provide a superior formula to F22, in that the calcium hydroxide would be converted to calcium oxide at 400^0C (cf. literature review 1.4.10) versus calcium carbonate at 825^0C. Due to the lower conversion temperature of calcium hydroxide to its oxide, it was presumed that all the calcium hydroxide in the formula would be converted to calcium oxide during the sintering of the core to 945^0C and thus would provide a superior disintegrating product compared to the calcium carbonate formula.

This appeared not to be the case; in fact the calcium carbonate formula produced a superior disintegrating formula by being more easily probed when using a sharp metal point than the calcium hydroxide formula. Although the shrinkage rate was higher than the calcium hydroxide formula (0,4%), it was still within the set limits, being 0,9%.

It must be noted that the calcium carbonate conversion to its oxide, is accompanied by a reduction in mass of 43,9% whereas the loss of mass of the calcium hydroxide is only 26.3% (cf. literature review 1.4.10).

From the mass loss factor stated above, it is assumed that perhaps the formulae with the calcium carbonate (F22) due to its greater loss of weight would make the core mass less dense and more porous when compared with F25. This weight loss factor making the core less dense and subsequently more porous could have been the reason that produced a core (F22) that was more easily penetrated as illustrated (cf. figure 3.7) when probed with the sharp metal point (albeit unproven).

3.8 Summary

It was deduced from the tests conducted in this chapter that formula F22 appeared to be the best formula by having a shrinkage value of 0,9% and a disintegrating time within 48 hours. However formula F25 had a shrinkage value of 0,6% and also disintegrated within 48 hours, but it had a disintegrated form that was made up of harder disintegrated mass than that produced from formula F22.

It was noted that formula F21 with double the amount of cement in its formula as compared with either F22 or F25 (cf. tables 3.1 and 3.5) also had promising results with a shrinkage value of 1% and a disintegrating time within 55 hours.

The choice to leave out formulae F23 and F24 in the next series of tests was in order to keep the investigation to within as few ingredient combinations as was deemed necessary and it was therefore decided to further compare formulae F21, F22 and F25 in sub-problem 3 under different conditions of relative humidity.

CHAPTER 4

EXPERIMENTAL PROCEDURES: SUB-PROBLEM 3

The experiments under review in this chapter were undertaken with a view to solve the following sub-problem

What are the relative humidity considerations that will facilitate the disintegration characteristics of a quick-setting core-body within the constraints of normal studio bronze casting procedures?

4.1 Foreword

The formulae F21, F22 and F25 were chosen as the most promising formulae for further investigation after considering the factors of shrinkage and disintegrating times investigated in the previous sub-problems.

These three formulae after having being fired to 945^0C (cf. sub-problem 1; foreword 2.1) were subjected to different humidity conditions and the results obtained from these observations are compared in table 4.1.

It must be understood that under general working conditions within a studio foundry in which newly cast bronzes (still contained within their outer ceramic shells and including their enclosed cores), stored for a while in normal studio environments are generally subject to fluctuations in ambient temperature and relative humidity. For the following relative humidity tests however, the relative humidity will be strictly controlled within the R H C apparatus and where the temperature can be kept fairly constant (cf. table 4.1). The relative humidity can be adjusted by introducing a water trough into the R H C apparatus or by leaving the water trough out of the R H C apparatus, in which case the surrounding relative humidity within the designated room (cf. def. of terms1.10.6) and thus inside the R H C apparatus will be recorded. A further set of tests will be conducted in which the naked test bars after having been fired to 945^0C will be kept within a refrigerator kept at 10^0C with a relative humidity of 74% for the duration of the disintegration test, namely for 48 hours.

4.2 Test one

The fired naked test bars, F21, F22 and F25 were subjected to the prevailing ambient temperature and relative humidity at the time of the test inside the R H C apparatus without the lid being in place (cf. def. of terms1.10.6). These values were between 19^0Cand 22^0C and at a relative humidity of between 74% and 78% respectively.

4.3 Test two

Another set of naked test bars, F21, F22 and F25 were placed in the second R H C apparatus with the lid in place where the relative humidity and ambient temperature was recorded at 81% and 20-21^0C respectively.

4.4 Test three

In test three, the core formulae (F21, F22 and F25) were subjected to a higher relative humidity in the third R H C apparatus containing a water trough (cf. methodology 1.5.13. 3). The temperatures were recorded at between 19^0C and 20^0C with a corresponding relative humidity at a constant 91%.

4.5 Test four

A further set of the three naked test bars were kept in the refrigerator at a constant 10^0C and at a constant relative humidity of 74%.

All the naked test bars in tests one to four were fired in the same kiln to 945^0C and were then immediately placed in their different environments as soon as they had cooled to room temperature. The test data was captured in table form illustrated in table 4.1.

	Test 1: F21, F22, F25	**Test 2**: F21, F22, F25	**Test 3:** F21, F22, F25	**Test 4:** F21, F22, F25
Elapsed time (hours)	Temp. 19^{0}-22^{0}C Relative humidity 74% - 78%	Temp. 20-21^{0}C Relative humidity 81%	Temp. 19^{0}–20^{0}C Relative humidity 91%	Temp. 10^{0}C Relative humidity 74%
6	Robust	Robust	Robust	Robust
12	Robust	Robust	Cracks appear	Robust
18	Robust	Cracks appear	Cracks appear	Robust
24	Cracks appear	Cracks appear	F21, F22, F25 Disintegrated	Robust
30	Cracks appear	Cracks appear		Robust
36 hours	Cracks appear	Disintegrated F22 and F25		Robust
42	Cracks appear			Robust
48	F22 and F25 disintegrated	F21 disintegrates		Robust
54	F21 disintegrated			Robust
60				Robust

Table 4.1 The disintegration times of Formulae F21, F22 and F25 at four different relative humidity values and the relevant results from the tests were recorded in the following table.

Tests	Test 1	Test 1	Test 1	Test 2	Test 2	Test 2	Test 3	Test 3	Test 3	Test 4	Test 4	Test 4
Formulae	F21	F22	F25	F21	F22	F25	F21	F22	F25	F21	F22	F25
Relative humidity	74%-78%	74%-78%	74%-78%	81%	81%	81%	91%	91%	91%	74%	74%	74%
Ambient temperature	19^{0}C – 22^{0}C	19^{0}C – 22^{0}C	19^{0}C – 22^{0}C	20^{0}C-21^{0}C	20^{0}C-21^{0}C	20^{0}C-21^{0}C	19^{0}C–20^{0}C	19^{0}C–20^{0}C	19^{0}C-20^{0}C	10^{0}C	10^{0}C	10^{0}C
Disintegration time (hours)	54	48	48	48	36	36	24	24	24	48 still robust after	48 still robust after	48 still robust after
Shrinkage %	1,0	O,9	0,6	1,0	O,9	0,6	1,0	0,9	0,6	1,0	O,9	0,6
Firing temperature 0C	945	945	945	945	945	945	945	945	945	945	945	945

Table 4.2 The results recorded in table 4.1

Results and discussion

4.6 Observations

4.6.1 Test one

Formulae F22 and F25 disintegrated within 48 hours into a granular composition, whilst F21 disintegrated later within 55 hours into a powdery composition. The granular particles of F25 were more difficult to crush between the fingers than F22, whilst the powdery composition of F21 was very soft. This factor is probably due to the fact that both F22 and F25 had half the parts by volume of cement than F21 (cf. table 3.1).

4.6.2 Test two

Formulae F22 and F25 disintegrated within 36 hours with a granular composition whilst F21 disintegrated within 48 hours into a powdery mass. The granular composition of F22 and F25 appeared to have an influence on the disintegrating times of the undisturbed naked test bars. F21 disintegrated into a fine powder which appeared to hold together for a longer period of time than the more granular compositions of formulae F22 and F25.

4.6.3 Test three

The three naked test bars were kept between21^{0}C and 22^{0}C with a relative humidity of 91% during the test. Within 24 hours, formula F21 had started to crack, being composed of large longitudinal as well as smaller lateral cracks. Formula F22 was just becoming soft at this stage with tiny little cracks appearing on its surface. After 24 hours all three formulae could be easily probed using a sharp metal point, the naked test bars all breaking down to a residue of powdery substance. Note that at higher relative humidity values i.e. 91%, the sintered naked test bars crumble and break down far more dramatically (cf. figure 4.1) than illustrated in the series in figure 3.1 which was photographed at a relative humidity of between 64% and 73%. The time of disintegration as in all cases was still taken from when the test bars first fell apart.

Figure 4.1 A photograph illustrating three naked test bars disintegrating inside the R H C apparatus.

The temperatures on the relative humidity thermometers were 22^0C for the dry bulb thermometer and 21^0C on the wet bulb thermometer. From tables the relative humidity was read off as 91% at these particular temperature readings.

4.6.4 Test four (in a refrigerator)

The set of formulae placed in the freezer that had a temperature of 10^0C with a relative humidity of 74%, showed no sign of disintegrating within 48 hours. The character of the tests remained the same as when they were first placed in the freezer. After 48 hours these test pieces were then removed from the freezer and place in an environment with an ambient temperature of 20^0C and a relative humidity of 80%. Within 48 hours these same pieces had disintegrated to a crumbly mass of powder.

4.7 Summary

The best results obtained for formulae F21, F22 and F25 appeared to be at the higher relative humidity at 91%. At this stage an interesting phenomenon presented itself. One would have expected the formulae to disintegrate rapidly when a mist of water was sprayed on to the fired test pieces as it is a well-known fact that when calcium oxide is moistened with cold water, there is a hissing sound emitted and the calcium oxide breaks and crumbles up into a powder of calcium hydroxide (cf. Holderness: 387). In the case of all the test formulae, this phenomenon did not occur. In fact, the converse happened. It appeared that it is essential in these test formulae that the disintegration process needs to be a slower reaction between the fired core material and the atmospheric humidity. The test pieces should not be allowed to become wet at this stage. Indeed, even a cursory exposure to even a mist of water (as produced by an atomizer) acts as a preventative in not allowing the fired test pieces to disintegrate. This phenomenon is most probably due to the fact that the plaster of paris becomes re-hydrated once again forming a firm mass.

The results for the three fired naked test bar formulae subjected to different relative humidity conditions indicated that the higher the relative humidity, the more rapid the disintegration of the undisturbed naked test bars within the R H C apparatus will be.

A decision was made that only F21 and F22 would be used to investigate sub-problem 4 in chapter 5, where the question would be asked how temperature affects the fired naked test bar.

Both formulae F21 (which became powdery on disintegration) and F22 (which became granular on disintegration) had calcium carbonate in their respective formulae. Formula F25 was made using calcium hydroxide and although the disintegration and shrinkage values for this formula (cf. table 4.2) were better than those obtained for formula F21, the nature of the disintegrated particles were of a harder nature than either F21 or F22 and it was felt that although the formula had disintegrated within the limits sought, it would be wise to keep the investigation to within as few ingredient combinations as was deemed necessary. It was therefore decided to use only formulae F21 and F22 in the following investigation in chapter 5.

CHAPTER 5

EXPERIMENTAL PROCEDURES: SUB-PROBLEM 4

The experiments under review in this chapter were undertaken with the view to solve the following sub-problem.

What are the temperature considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal ceramic shell sintering parameters?

5.1 Foreword

The experiments under review for this chapter were to consider a range of temperature requirements within the ceramic shell process, and are discussed are as follows:

The ceramic shell is normally sintered to between 900^{0}C and 1000^{0}C, to produce a strong, robust ceramic structure that can withstand the bronze casting process.

The temperatures that were selected to ascertain the optimum sintering parameters for a specific test core formula, namely formulae F21 and F22, are recorded in the following tables, 5.1 and 5.2. In all the experiments to date, all the test pieces had been fired to 945^{0}C, which had been selected as an intermediate temperature between 900^{0}C and 1000^{0}C.

5.2 Test method

The two sets of test formulae (in the form of naked test bars), F21 and F22 were fired at the same time in three different but similar test kilns to 900^{0}C (Orton cone 010), 945^{0}C (Orton cone 08) and 1000^{0}C (Orton cone 06) and allowed to cool within their respective kilns, after each of the tests had reached their firing temperatures. The naked test bars were then removed and placed in one of the two R H C apparatuses where the conditions of relative humidity was either at 91% at 20-21^{0}C or 81% at 21^{0}C respectively. A comparative discussion on the merits of the different relative humidity values and how they affected the disintegrating times of the test pieces fired to 900^{0}C, 945^{0}C and 1000^{0}C is discussed after table 5.2.

Results and discussion

Firing temperature	**900^{0}C cone 010**	**945^{0}C cone 08**	**1000^{0}C cone 06**
Disintegration time F21	Within 48 hours powder	Within 48 hours soft powder	Within 48 hours very soft powder
Disintegration time F22	Within 48 hours granular	Within 36 hours soft and granular	Within 36 hours very soft and granular
Relative humidity	81%	81%	81%
R H C apparatus temperature	19-20^{0}C	19-20^{0}C	19-20^{0}C
Shrinkage F21	0,9%	1,0%	1,0%
Shrinkage F22	0,8%	0,9%	0,9%

Table 5.1 The relationships between temperature, relative humidity and disintegration.

Firing temperature	**900^{0}C cone 010**	**945^{0}C cone 08**	**1000^{0}C cone 06**
Disintegration time F21	36 hours-fine powdery mass	24 hours-fine soft powdery mass	24 hours-fine very soft powdery mass
Disintegration time F22	30 hours fine granular mass	24 hours fine soft granular mass	24 hours fine very soft granular mass
Relative humidity	91%	91%	91%
R H C apparatus temperature	20-21^{0}C	20-21^{0}C	20-21^{0}C
Shrinkage F21	0,9%	1,0%	1,0%
Shrinkage F22	0,8%	0,9%	0,9%

Table 5.2 The relationships between temperature, relative humidity and disintegration.

5.3 Discussion of table 5.2

A comparison between the two formulae, namely F21 and F22 fired to the three temperatures of 900^{0}C, 945^{0}C and 1000^{0}C and then subjected to a relative humidity of either 91% or 81%, showed a large difference in the disintegrating times. A relative humidity of 91% showed that at this high percentage, the formulae disintegrated more rapidly than at lower relative humidity values. The times for disintegration at different sintered temperatures for each of the two formulae were different but it was the relative humidity that played a decisive role in the disintegration of the test pieces.

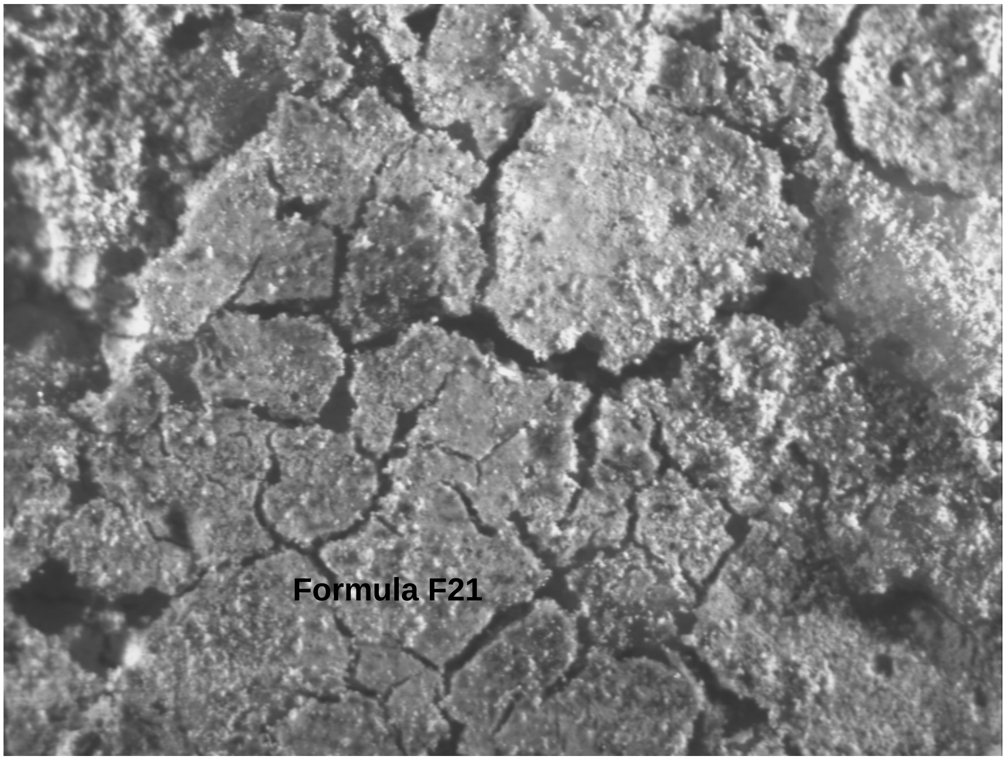


Figure 5.1 A close-up photograph of the fired surface of formula F21 to illustrate the cracks that appeared on the surface shortly before it broke down as recorded in figure 5.2 below.

Just prior to the naked test bars falling apart (disintegrating) these surface cracks became even larger and the whole structure becomes a mass of small granules, which are very powdery when pressed between the fingers (especially in the case of F21).

The following photograph illustrates formulae F21 and F22 breaking up into a powdery mass for F21 and granules for F22 when fired to 900^0C.

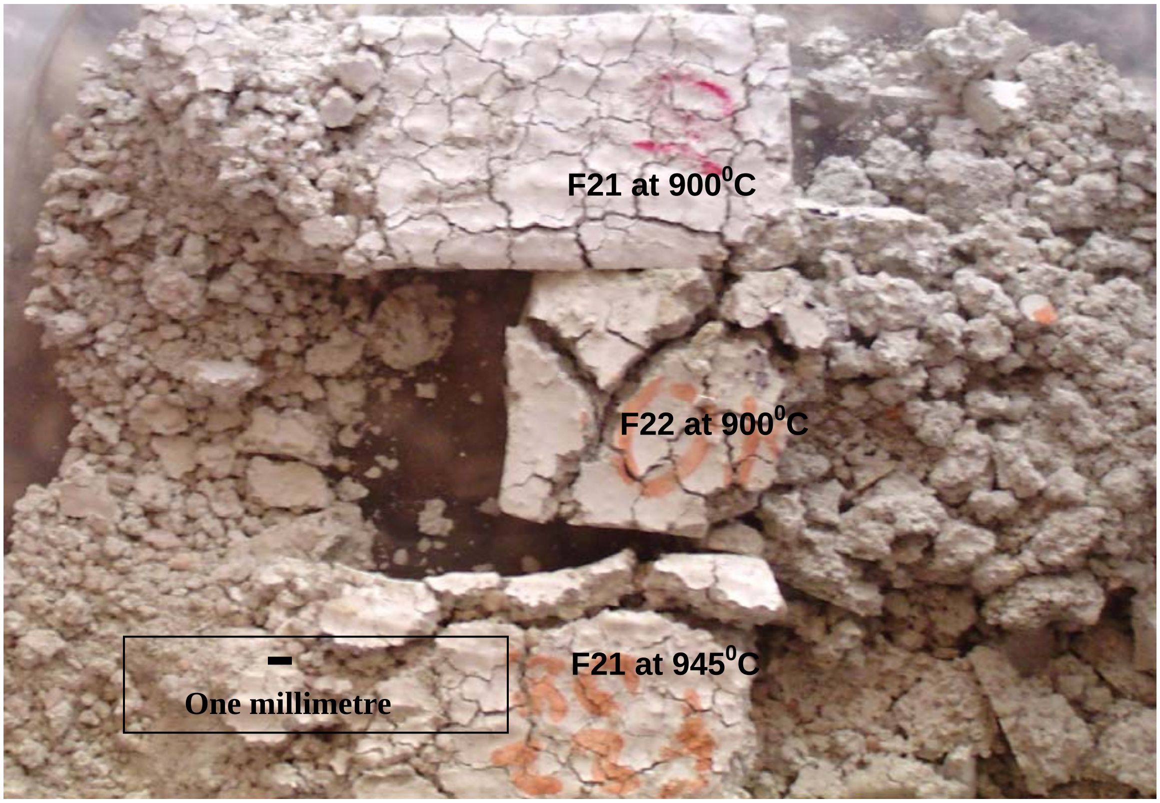


Figure 5.2 In the photograph above (which illustrates the facts recorded in table 5.1), the top left-hand corner of the photograph shows formula F21 that has been fired to cone 010 (900^{0}C) and kept at a relative humidity of 81% at a temperature of between 20-21^{0}C, which disintegrated within 48 hours.

The photograph also reveals that the naked test bar has broken down into fine granules approximately 1mm in diameter which could be easily powdered between the fingers. The disintegrating test bar in the middle of the photograph, illustrates formula F22 that has also been fired to 900^{0}C and kept under the same conditions as formula F21 above. Here the photograph illustrates that formula F22 had disintegrated into harder granular shapes approximately 5 mm in diameter which did not powder very easily when pressed between the fingers.

In the bottom half of the photograph, another naked test bar, formula F21 is illustrated when beginning to break down to a powder sized particles, but here the test bar has been fired to the higher temperature of 945^{0}C (cone 08).

5.4 Observations

5.4.1 Tests at 900^0C

The two test formulae F21 and F22 were both fired to 900^0C and after the kiln reached this temperature, the test samples were allowed to cool within the kiln for 4,5 hours (this is the natural cooling cycle of the test kilns in use at the PET), before being removed. The test pieces were immediately placed in their respective environments, that is, one set of samples were subjected to a 91% relative humidity and the other set of samples were subjected to a relative humidity of 81%. The disintegration of both sets of naked test bars occurred within 48 hours. The disintegrated test bars had an irregular granulated surface appearance, each granule approximately 1 mm in diameter for formula F21 and 5 mm for formula F22. When these granules were compressed between the fingers, they easily broke down to a fine powder.

5.4.2 Tests at 945^0C

The test formulae F21 and F22 after being fired to 945^0C were subjected to the same conditions as the tests conducted at 900^0C, namely, at either a relative humidity of 81% or 91% (cf. table 5.1 and 5.2). The disintegration times were very similar to the tests conducted at 900^0C, except that F22 now disintegrated within 36 hours. These test bars also broke down to a fine powdery mass with F21 being the softer of the two when pressed between the fingers. Note: in chapter 3; table 3.1, formulae F21 and F22 when fired to 945^0C and kept at a relative humidity of between 64% and 73% inside the R H C apparatus disintegrated only after 55 hours and 48 hours respectively. The shrinkage rate was also similar to the test conducted at 900^0C.

5.4.3 Tests at 1000^0C

The two test formulae (F21 and F22) after firing to 1000^0C were again subjected to a relative humidity of either 91% or 81%. The results showed that the shrinkage percentages had increased slightly for both formulae from when they fired between 900^0C to 1000^0C with an increase in shrinkage of 0.1% respectively. There was comparatively little to choose between the formulae when fired between 945^{0}C and 1000^{0}C, with reference to disintegration results at each particular relative humidity.

5.5 Summary

Firstly, from the results of the tests conducted above, the firing temperature of between 900^{0}C and 1000^{0}C for the core formulae F21 and F22 showed very little difference in the shrinkage values,

Secondly, the relative humidity appeared to play a major role in the characteristics of the disintegrating naked test bars. A high relative humidity of 91% had an accelerating effect on the disintegration as compared with a relative humidity of 81%,

Thirdly, the firing temperature did increase the rate of disintegration of the fired naked test bars as the temperature was raised from 900^{0}C to 1000^{0}C.

These three temperature considerations will be taken cognizance of in the following sub-problem 5, where cores for use in actual bronze pours will be used.

Once again (cf. summary: chapter 4) a decision was made to keep the investigation to within as few ingredient combinations as was deemed necessary. It was decided therefore to advance formula F21 to the bronze casting procedures in chapter 6, due to its powdery and thus more homogenous physical nature, after being fired to various temperatures and subsequent exposure to the different relative humidity conditions.

CHAPTER 6

EXPERIMENTAL PROCEDURES: SUB-PROBLEM 5

The experiments under review in this chapter were undertaken with the view to solve the following sub-problem.

Would the conclusions inferred in the first four sub-problems be applicable to core formula/formulae when used for the actual production of a wide range of hollow bronze casts?

6.1 Foreword

6.1.1 The parameters

The parameters determined in the first four sub-problems are briefly reviewed here to determine whether they would be applicable to a core-body formula when used in a wide range of hollow bronze casts.

In sub-problem 1, (where the choice of materials were evaluated), it was determined that four materials would constitute the core formula in various combinations; these being cement, calcium carbonate, plaster of paris and silica. This sub-problem was finally addressed with the production of formula F17.

In addressing sub-problem two, it was found that three formulae had parameters that complied with the limits set for disintegrating times (disintegration within 48 hours) and for shrinkage values equal to or less than 1%. These were formulae F21, F22 and F25.

Whilst investigating sub-problem three, the three formulae F21, F22 and F25 were further evaluated when regarding relative humidity versus disintegration times. It was found that the higher the relative humidity (tested between 73% and 91%), the more quickly the naked test bars disintegrated.

Formulae F21 and F22 proved to be the most successful formulae at this stage of the investigation.

When investigating temperature versus disintegration time in sub-problem four, the two formulae F21 and F22 were tested at all three temperatures, namely; 900^{0}C, 945^{0}C and 1000^{0}C respectively. Of the two remaining formulae (F21 and F22), formula F21 was chosen as the more promising of the two. Although they both had similar shrinkage values, they had dissimilar post-fired characteristics. In this regard, formula F21 disintegrated into a fine powder whilst formula F22 broke up into large granular pieces that although softer than F25, they did not break into a fine powder as easily as F21 (cf. figure 5.2). It was decided that as F21 disintegrated into a powder it would be the formula of choice for further investigation as a core-body formula in real life bronze casting procedures.

At this stage of the investigation, all the naked test bars (i.e. tests F1 – F25) only measured 100 mm x 20 mm x 20 mm (40 ml). This was done for two main reasons, namely:

- For use in the Hounsfield compression test apparatus (cf. methodology 1.5.8);
- It would have been premature to analyse the possible impact that larger core volumes may have had on disintegration efficacy at this primary testing phase.

However, it now became critical to determine whether the volume of core material played a role in the disintegrating characteristics of formula F21, as larger volumes of core material would be used in the bronze casting tests. A series of three consecutive tests were conducted as described below, to verify whether larger naked test bars in the form of naked test bricks would alter the conditions of disintegration noted before in chapters three and four.

Results and discussion

6.1.2 Test to determine whether volume affects the disintegration characteristics of formula F21 when using either the naked test bars or naked test bricks

To investigate this volume phenomenon, three similar consecutive tests were conducted as described in the test below.

Nine bricks with the dimensions of 200 mm x 100 mm x 50 mm (1000 ml) and nine test bars with the dimensions of 100 mm x 20 mm x 20 mm (40 ml) were made using formula F21.

The naked test bricks together with the naked test bars were cured for seven days under similar conditions of temperature and relative humidity. They were then divided into three groups. Each group was fired to one of the following temperatures: 900^0C, 945^0C and 1000^0C. One brick and one naked test bar from each group was kept in one of three R H C apparatuses where the relative humidity was kept at 91%, 81% to 84% and 73% (cf. table 4.2, which this test replicates as closely as possible). The reader is reminded that these relative humidity controls are subject to the prevailing temperature of the day which in this instance was recorded at 22^0C (cf. def. of terms, R H C apparatus 1.10.6). The results for the three consecutive tests are recorded in the following table 6.1:

Formula F21	**Test at 91% relative humidity**	**Test at 81% - 84% relative humidity**	**Approximate 73% relative humidity**
Naked test brick, repeated 1000^0C	Disintegrating times Within 24 hours	Disintegrating times Within 36 hours	Disintegrating times Within 40 hours
Naked test brick, repeated 945^0C	Disintegrating times Within 24 hours	Disintegrating times Within 36 hours	Disintegrating times Within 40 hours
Naked test brick, repeated 900^0C	Disintegrating times Within 24 hours	Disintegrating times Within 36 hours	Disintegrating times Within 40 hours
Naked test bar, repeated 3x 1000^0C	Disintegrating times Within 24 hours	Disintegrating times Within 36 hours	Disintegrating times Within 40 hours
Naked test bar repeated 945^0C	Disintegrating times Within 24 hours	Disintegrating times Within 36 hours	Disintegrating times Within 40 hours
Naked test bar repeated 900^0C	Disintegrating times Within 24 hours	Disintegrating times Within 36 hours	Disintegrating times Within 40 hours

Table 6.1 The disintegrating times of the naked test bars and the larger volume naked test bricks at three different relative humidity settings.

6.1.3 Summary for tests conducted in 6.12

The results observed for the naked test bars and the naked test bricks were very similar in their disintegrating characteristics at the three relative humidity settings. Perhaps with larger volumes a difference would become apparent, but this is beyond the scope of cores tested for general use in a small bronze art foundry.

6.2 Introduction to the experiments to investigate core formulations

Seven experiments were conducted to investigate the problem of whether the conclusions inferred in the first four sub-problems would be applicable to the further development of a core-body that would be suitable when used in a wide range hollow bronze casts.

A series of experiments were conducted beginning with an initial investigation of the properties of formula F21 as a core-body in real-life bronze casting conditions. The methods of the investigations would follow an empirical testing sequence which would be based on the results obtained in each preceding experiment conducted in this chapter. Testing would be continued until a final formula had been developed that would be suitable as a core-body for a wide range of hollow bronze casts (cf. def. of terms: wide range of hollow bronze casts, 1.10.7).

6.3 Experiment 1 To examine the disintegrating characteristics of core formula F21 within a cast bronze at a relative humidity of 91%, 81% and 73%.

6.3.1 Method

Three hollow wax tubes with the dimensions of 300 mm x 30 mm were filled with the core formula F21 (2 parts of cement, 2 parts of calcium carbonate, 1 part of plaster of paris and 2 parts of silica (0,95 mm) mixed with 2,5 parts of de-ionized water to produce a pourable mass; cf. def. of terms 1.10.4). After waiting for six hours to allow the cores to set within the wax moulds, the wax tubes were invested in the ceramic shell and were allowed to cure for seven days (cf. delimitations 1.6.5).

After the seven-day curing period, the three invested moulds were placed in an electric kiln and were de-waxed at approximately 600^0C, and were subsequently sintered (with the three naked test bars depicted in figure 6.1), to 945^0C, being the median temperature of the experiments for the naked test bars in the previous four sub-problems (cf. temperature in the methodology 1.5.18.2).

Figure 6.1 A photograph of three wax tubes 300 mm x 30 mm that were filled with core formula F21, invested in the ceramic shell and sintered with the three naked test bars depicted in the photograph before being cast in bronze.

The hot ceramic moulds containing the cores were removed from the kiln and were then cast in bronze at approximately 1200^{0}C. After the moulds had cooled to room temperature, one mould with one of the naked test bars (as a control) was placed in a R H C apparatus, (which included a water trough), at 91% relative humidity (cf. methodology 1.5.13). The second mould with a naked test bar (as a control) was placed in another R H C apparatus without a water trough where the relative humidity was at 81% and the third mould and the naked test bar were placed in a third R H C apparatus without a lid where the relative humidity at the time of the test was close to 73%.

6.3.2 Observations

A long screwdriver was used as a gouging tool (approximately every six hours) to try and dislodge the cores from within the bronze casts. The dislodging of the cores from their respective bronze casts at the three relative humidity values showed no great variation from one other. As predicted the naked test bars proved to behave as before in the tests in sub-problem 3 (cf. table 4.1), where the naked test bar at the higher relative humidity of 91%, disintegrated within 24 hours, the naked test bar at 81% disintegrated within 36 hours whilst the naked test bar kept at approximately 73% relative humidity, disintegrated within 40 hours (cf. methodology 1.5.13).

The core material inside the hollow bronze cast tubes did not disintegrate into loose masses (as was the case with the naked test bars) and further could not be simply poured from the bronze casts but had to be independently gouged out of the casts. Remnants of the core were intentionally left inside the bronze (which were still easy to remove) to determine whether the core would break down further in time which would then allow the core to be simply poured from the cast bronze. In fact no further developments ensued. The core remnants did however appear to become more easily dislodged when left undisturbed after forty-eight hours and even more so over an extended period of time (seven days) but they still had to be gouged out from the cast tubes. These factors indicated that the formula, in the form of the naked test bars was behaving differently when used within an actual bronze cast, perhaps due to a matter of a diffusion-control-led reaction. Inside the tubes access of air ingress would be restricted compared to the open naked bars.

Further testing (experiment 2) of core formula F21, in a larger mould was subsequently performed (female torso) in the hope that the larger internal surfaces of the hollow mould would make it easier to remove the core from the cast bronze, and this in turn may have provided a clearer indication as to why the formula F21 performed so well as a naked test core in sub problems two, three and four, yet failed to give satisfactory disintegrating results in the bronze cast scenario when used as a core in a long narrow bronze cast, 300 mm x 30 mm.

6.4 Experiment 2 To examine the disintegrating characteristics of formula F21 at a relative humidity of 91% when used as a core in the hollow wax female torso in the bronze casting process.

Figure 6.2 A photograph of the wax female torso 300 mm tall illustrating the core pins that were inserted into the wax prior to the core being poured into the hollow mould.

6.4.1 Method

The core formula F21 was prepared as described in experiment 1 (paragraph 6.3) and subsequently poured into the wax female torso mould. Vent holes 15 mm in diameter were made in the core using a straight length of 15 mm copper water pipe. A thermocouple would be inserted into one of the vent holes during the sintering process and when the temperature inside the core had reached the required temperature (which took approximately half an hour of soaking in the kiln in each case) the kiln would be switched off (cf. sintering and thermocouple control in the methodology 1.5.18). Three naked test bars were made using formula F21 to compare the reaction of the formula in a naked test bars against the formula inside a bronze cast.

After investing the mould in the ceramic shell and waiting for the prescribed seven-day curing period, the mould was de-waxed and sintered to 945^0C. Molten bronze was then poured into the hollow mould and the mould was allowed to cool to room temperature. The mould was placed in a R H C apparatus where the relative humidity was at 91% (cf. figure 6.3).

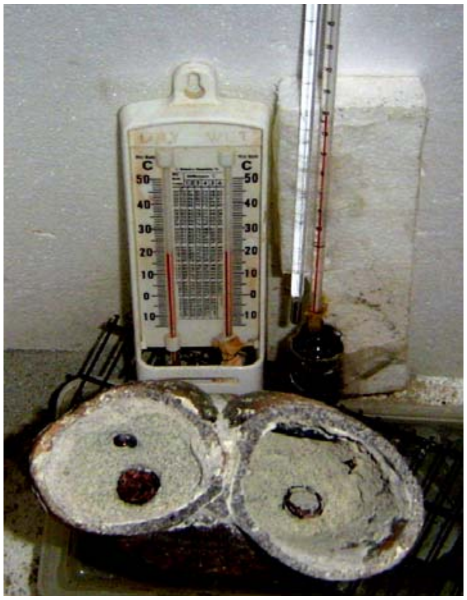


Figure 6.3 A photograph illustrating the bottom view of the 300 mm tall female torso bronze mould placed in the R H C apparatus on a metal grid which covers the water trough. A relative humidity instrument stands behind the bronze torso.

6.4.2 Observations

F21 in the form of a naked test bar could be easily broken down within thirty minutes after having been fired to 945^{0}C and then cooled to room temperature. However, only after twenty hours in the R H C apparatus (where the core inside the female torso mould was left undisturbed) did the core begin to show signs of disintegration. The core could now be pried away and dislodged (but not easily) from the bronze cast. However, it was noted that the core did became easier to remove from the interior of the larger female torso mould when compared to the long narrow tube moulds in experiment 6.1.

It was noted when dislodging the core from the bronze cast that the core material had already disintegrated and it was considered that it was perhaps the silica particles that were somehow lodged tightly between the disintegrated material within the confines of the mould, that was preventing the core from being easily removed (albeit unproved). Once again the naked test bars made from formula F21 and fired to the same temperature as the female torso core, behaved as previously recorded in table 4.1, chapter 3, by disintegrating within 24 hours when left undisturbed inside the R H C apparatus.

Figure 6.4 A photograph of the 300 mm bronze cast female torso that was filled with core formula F21.

The core was difficult to dislodge from the hollow bronze even when kept in an atmosphere at 91% relative humidity.

Core formula F21 was proving not to be the ideal disintegrating core formula due to the difficulties in removing it from the hollow bronze casts. Parameters from previous experiments in sub-problems three and four were subsequently reviewed with the intention of modifying or improving formula F21, so that it could be easily removed from its bronze cast.

6.4.3 Review of previous experiments

Reviewed in sub-problem two; table 3.3 illustrated that formulae F22, F23 and F24 had three parts, four parts and five parts of silica in their respective formulae. It must be remembered however, that in these three formulae, the cement content was at one part per volume as opposed to two parts per volume in formula F21. The main observation that was made in table 3.3 (chapter 3) using formulae F22, F23 and F24, was that as the silica content was increased, so the fired naked test bars became weaker. The reason for the formulae becoming weaker as the silica content was increased is probably due to the fact that as the silica content was increased, so the ratio of the other materials in the formula were proportionately reduced as well as the fact that the fired powder mass of the formula does not adhere to the silica particles. This combined effect may cause the weakening the whole fired structure.

In the photograph (figure 6.5) below, it will be noted that the disintegrated powder mass of fired formula F21 (consisting of cement, calcium carbonate and plaster of paris) does not adhere to the silica particles but merely lies on top of them and can be easily dusted from these silica particles.

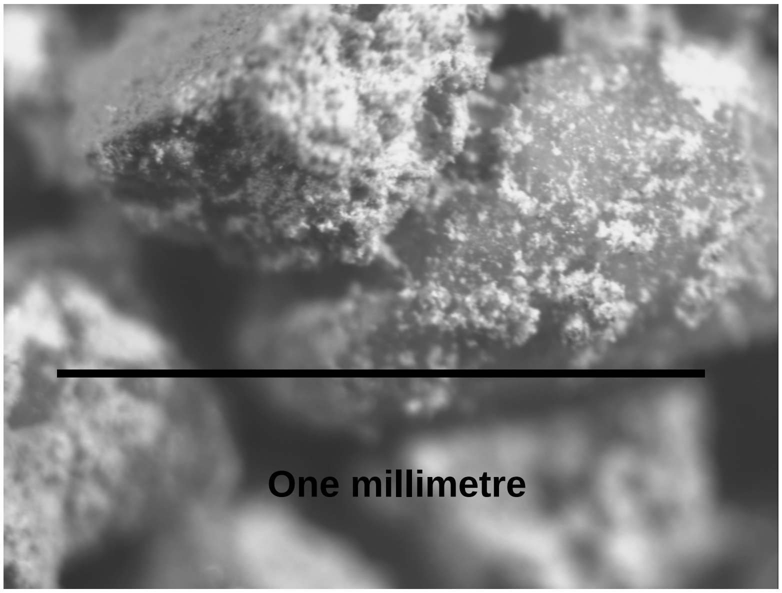


Figure 6.5 A microscopic photograph of the fired formula mass F21, illustrating the fine disintegrated powder that does not adhere to the silica particles.

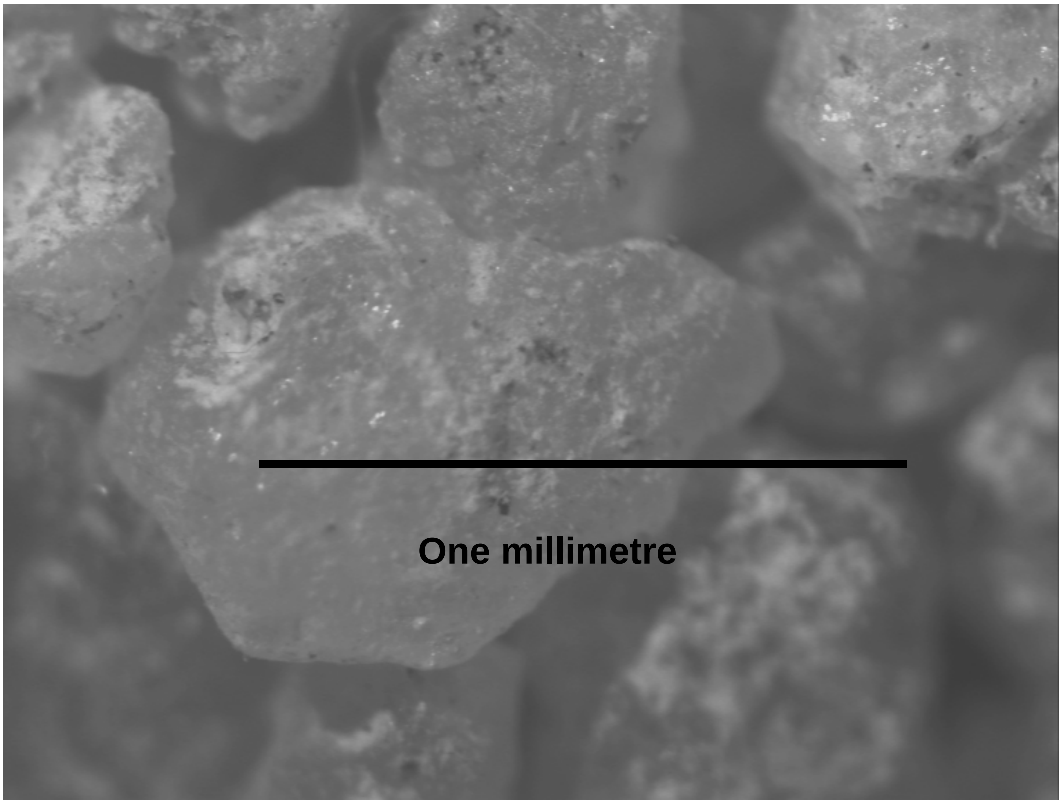


Figure 6.6 A microscopic photograph of the silica particles, dusted free of the loose disintegrated powder illustrated in Figure 6.5 above.

6.4.4 Further investigations

To reiterate, the reason for increasing the silica content in the modification of formula F21 was deduced from the fact that in experiments conducted on formulae F22, F23 and F24 (cf. table 3.3; chapter 3) that as the silica content was incrementally increased, so the formulae became weaker or broke down more easily, in essence, they became more friable. Another pertinent factor relating to formulae F22, F23 and F24 was that as the ratio of the silica content was increased (with a subsequent proportional reduction of the three other materials in the formula) so the shrinkage values decreased as indicated below.

F22 = 3 parts of silica with a shrinkage value of 0,9%
F23 = 4 parts of silica with a shrinkage value of 0,7%
F24 = 5 parts of silica with a shrinkage value of 0,4%

The photograph below has been included to illustrate the nature of the fired mass of silica particles lodged amongst the disintegrated powders of cement, calcium carbonate and plaster of paris.

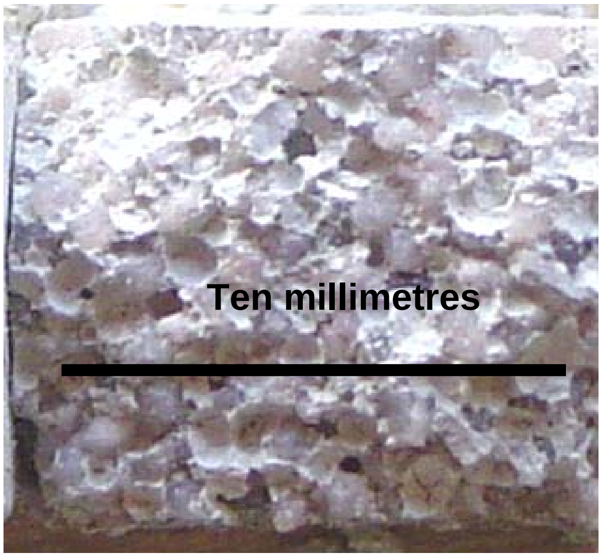


Figure 6.7 A photograph of the fired naked test bar, F21. Note the silica particles amongst the fired material of cement, calcium carbonate and plaster of paris. The cratered appearance is due to silica particles having fallen away from the loose surface of the naked test bar.

Theoretically, by incrementally increasing the silica content in formula F21, two variables should alter, namely the core should break down more readily and the shrinkage values should decrease (as was found in F22, F23 and F24). Following this logic, the following experiment was conducted where silica was added in incremental steps to formula F21.

6.5 Experiment 3 To examine the disintegrating characteristics of formula F21, F21A, F21B, F21C, F21D, F21E, F21F and F21G tested at a general relative humidity of 73% and 91% when used as cores in hollow wax tubes (300 mm x 30 mm) cast in bronze.

The relative humidity in experiment 1(paragraph 6.3) and experiment 2 (paragraph 6.4) had no apparent effect on the dislodging of the cores from the cast bronzes and so it was decided to investigate with pragmatism how the modified formulae F21A to F21G and including F21 behaved at a lower and a higher relative humidity. If a marked difference was detected in the disintegrating times then further experiments would be conducted to determine more detailed relative humidity parameters on the disintegration of the core within a cast bronze.

6.5.1 Method

Sixteen cast wax tubes, 300 mm x 30 mm, were divided into two equal groups. Each wax tube from each group had one of the formulae (detailed below in table 6.1) poured into it. These cored tubes were then invested in the ceramic shell and sintered to 945^0C with their corresponding naked test bar counterparts. The tubes were subsequently cast in bronze. Each formula within the two cast groups with the corresponding naked test bar formula (as a comparative control) was either placed in a R H C apparatus kept at a general relative humidity at 73% or 91% (cf. delimitations relative humidity 1.6.12).

6.5.2 Observations

Table 6.2 records the formulae mix proportions of the ingredients used to make up formulae F21 and F21A to F21G illustrating the volume of water that should be added to each formula to achieve a pourable mix that is not either too dry or too wet to achieve a core-body with the minimum of air pockets in the wet mix.

Formula	**F21**	**F21A**	**F21B**	**F21C**	**F21D**	**F21E**	**F21F**	**F21G**
Cement	2	2	2	2	2	2	2	2
Calcium carbonate	2	2	2	2	2	2	2	2
Plaster of paris	1	1	1	1	1	1	1	1
Silica 0,95 mm	2	3	4	5	6	7	8	9
De-ionized water	For a pourable mass add 2.5	For a pourable mass add 2.6	For a pourable mass add 2.7	For a pourable mass add 2.8	For a pourable mass add 2.9	For a pourable mass add 3.0	For a pourable mass add 3.1	For a pourable mass add 3.2

Table 6.2 The formula series that were made for this experiment.

The addition of water is a variable in the formulae in that as the silica is increased in each consecutive formula, so the water requirement has to be increased slightly to accommodate the additional silica content in the formulae. This amount of water that is required to be added to achieve a pourable mass has been closely monitored, as a small addition over and above that stated in the table above, results in a runny mix. It is desirable to add the least amount of water to achieve a pourable mass as this water has to be evaporated off in the de-wax process (cf. def. of terms 1.10.4 pourable mass).

The following photograph illustrates one group of hollow wax tubes each which has a particular core formula poured into it. The corresponding naked test bars were used for comparative purposes to determine how the modified core formulae would behave as naked test cores as well as determining their shrinkage values and their sintered compression values measured on the Hounsfield apparatus (cf. methodology 1.5.10).

Figure 6.8 A photograph of one group of hollow wax tubes 300 mm x 30 mm with naked test bars as comparative controls having the same formulae that was poured into the corresponding wax tube.

To reiterate, in experiment 1 (paragraph 6.3) hollow tubes and naked test bars as illustrated in figure 6.1 were used to test F21. It was found that the naked test bars behaved as expected but the same formula (F21) inside the hollow tubes appeared to bind inside the tubes and had to be gouged out of the bronze casts. It was therefore decided to repeat the same testing format using the narrow wax tubes for the modified F21 tests in this experiment.

The series of naked test bars (as illustrated) positioned above the wax moulds in figure 6.8 were fired together with each group of core tests to 945^0C. The figures recorded in table 6.3 below, were for the results obtained in the comparative naked test bar assessment.

Formula	F21	F21A	F21B	F21C	F21D	F21E	F21F	F21G
shrinkage	0,9%	0,8%	0,8%	0,6%	0,2%	0,2%	0,2%	0,1%
Silica	2	3	4	5	6	7	8	9

content	parts	parts	parts	parts	parts	parts	parts	parts
Disinte-gating times 73% relative humidity	40 hours	36 hours	36 hours	30 hours	24^{+} hours	24^{+} hours	24^{+} hours	20 hours
Disinte-gating times 91% relative humidity	24 hours	24 hours	24 hours	20 hours	20^{+} hours	20^{+} hours	20^{+} hours	20 hours

Table 6.3 records the disintegrating times for the naked test bars when fired to 945^{0}C. The super-script + sign next to formulae F21D, F21E and F21F highlights the fact that the properties for these formulae are very similar and will be taken cognizance of in future experiments.

In table 6.3, it was noted (at a relative humidity of 73%) that formulae F21 to F21C broke down when undisturbed between 40 and 30 hours, whilst formulae F21D to F21F all broke down within twenty-four hours whilst F21G broke down after twenty hours. At 91% relative humidity the disintegrating times were reduced for all the tests which bears out similar results recorded in table 6.1 in the tests for relative humidity for F21. The shrinkage values of the formulae F21 to F21G were reduced as the silica content was increased in the formulae. Further, the disintegrating rates for the formulae containing the higher values of silica were also reduced.

6.5.3 A series of photographs illustrate the characteristics of naked test bar F21D that disintegrating over 24 hours

The following series of photographs, figures 6.9 to 6.12, illustrated formula F21D slowly disintegrating when left undisturbed after being fired to 945^{0}C and kept in the R H C apparatus at 20^{0}C with a relative humidity of 73% (cf. table 6.3)

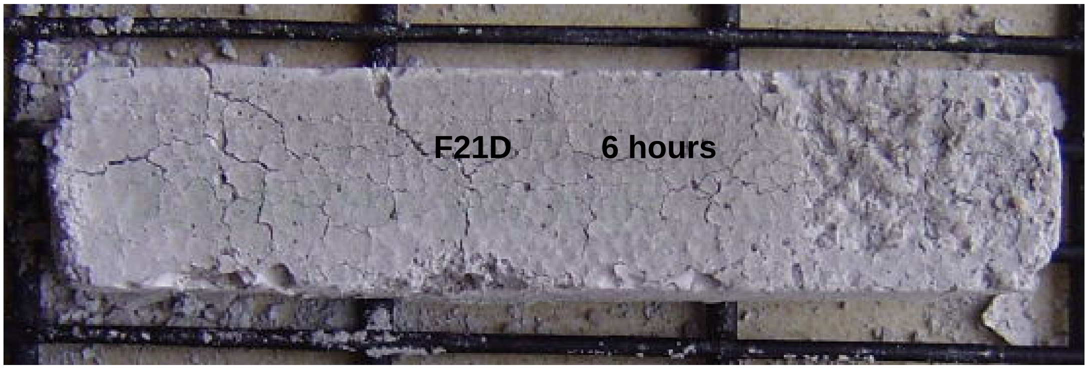


Figure 6.9 An enlarged photograph of naked test bar F21D, 6 hours after being removed from the kiln.

Notice that a few particles lying below the metal grid in the R H C apparatus had broken from the undisturbed test bar at this time, which although it remained intact when left undisturbed, it could be easily broken when touched.

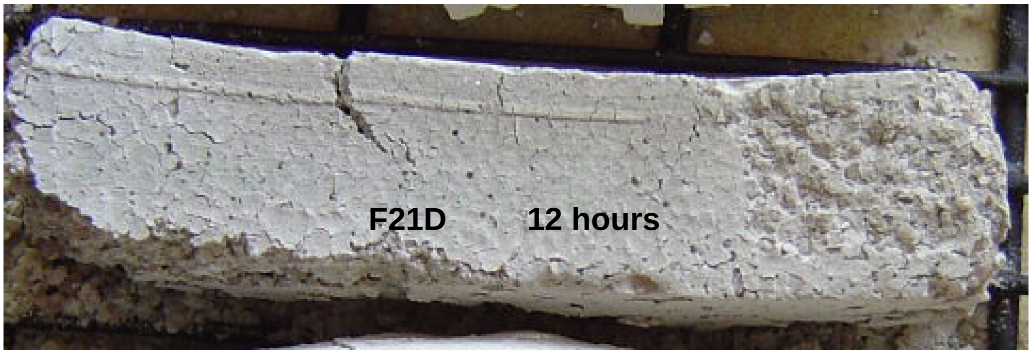


Figure 6.10 An enlarged photograph of naked test bar F21D, 12 hours after being fired.

The surface cracks slowly began to increase in size as the naked test bar began to disintegrate.

Figure 6.11 A photograph of formula F21D, 18 hours after being fired.

The test bar was already in a very crumbly condition and it was only the compacted surface that appeared to prevent the mass from collapsing completely.

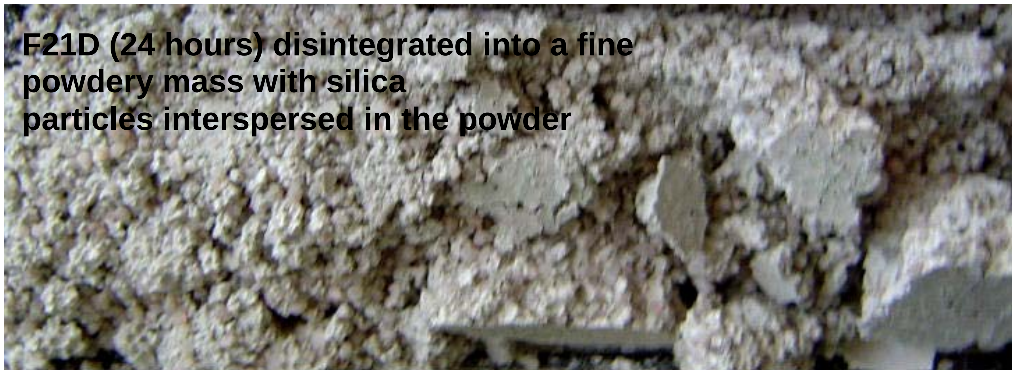


Figure 6.12 A photograph of formula F21D, 24 hours after being fired.

When the test bar was lightly touched it immediately crumbled into a fine powdery mass illustrated above. A further phenomenon that was observed here, was that once the naked test bars had cooled to room temperature and were then gently tapped they could be easily broken down as illustrated in figure 6.12. This was in contrast to all the previous tests conducted on naked test bars where the test bars were left to disintegrate undisturbed (cf. sub-problems two, three and four).

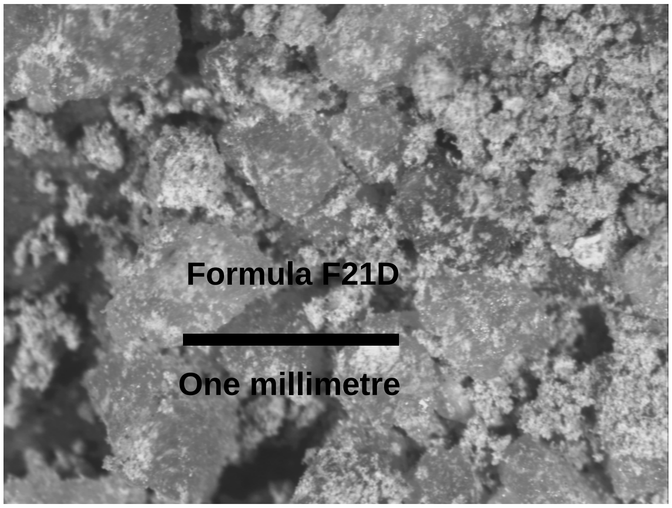


Figure 6.13 A magnified photograph of formula F21D (from figure 6.12) illustrating the nature of the disintegrated powders (cement, calcium carbonate and plaster of paris) lying loosely on the 0,95 silica particles.

6.5.4 Compression tests

Compression tests were conducted to establish the degree by which the naked test bars became weaker as the silica content was increased in the formulae.

The compression test results for the eight naked test bars tests tabled in 6.4 below, highlighted a problem with using the Hounsfield testing apparatus. The results listed in this table were obtained from successively testing each formula six times. The results however only indicated that formula F21 had a greater compressive strength than formula F21G (cf. table 6.4). On closely examining each test bar and also by scratching away the surface layer, it could be seen in the underlying mass that the numerous particles of silica (0,95 mm) were not homogenously spaced in the mix. Six consecutive compression tests for each of these sintered naked test bars could not be verified to any degree of accuracy and the results shown below are merely an indication that a trend was observed in that the sintered naked test bars became progressively weaker as the silica content was increased, which was in line with the disintegration times observed in table 6.3 above.

Formula	F21	F21A	F21B	F21C	F21D	F21E	F21F	F21G
Approx. fired strength	4.0 MPa	4.0 MPa	4.0 MPa	3.0 MPa	3.5 MPa	3.0 MPa	3.0 MPa	2.0 MPa

Table 6.4 The sintered compression figures derived from the tests using the Hounsfield compression apparatus could be linked to the fragility or the binding strengths of the sintered formulae.

6.5.5 Summary

There was no apparent difference that could be determined between the eight formulae (F21and F21A to F21G) and their disintegration properties at the two different relative humidity settings of 73% and 91%, except that the core appeared to become less difficult to remove as the silica content was increased. It was also found that the cores could be dislodged from the hollow bronzes as soon as the bronze cast had cooled to room temperature. Here, there was no noticeable difference when removing the cores from bronzes that had just reached room temperature and those which had remained in the R H C apparatus. Once again as in sub-problem 4, it was the naked test bars that showed the positive effects of relative humidity on disintegrating times as recorded in table 6.3.

However core formula F21G appeared to have the best core removal properties from those tested above. Formula F21G was therefore selected to be tested as the core body in experiment 4 (paragraph 6.6) below.

6.6 Experiment 4 To evaluate the disintegrating characteristics of core formula F21G in a bronze casting, using the female torso as a model.

6.6.1 Method

Formula F21G was mixed with 3,2 parts by volume of de-ionized water to make a pourable mix which was then poured into the female torso wax mould and invested in the ceramic shell and cast in bronze as described in experiment 1(paragraph 6.3). The outer exposed area of the core, where the pouring cup meets the mould, was found to be very fragile after being sintered to 945^0C (this factor was not noticeable in the much smaller exposed core when using a long narrow tube 300 mm x 30 mm, in experiment 6.3 (paragraph 6.5). Molten bronze was poured into the mould and on cooling the core could be very easily dislodged by simply gouging the core away using a long screwdriver (cf. figure 6.14).

Figure 6.14 A photograph shows the ease with which core F21G was removed from the bronze female torso.

A long screwdriver could be easily inserted up to its hilt into the core. Unfortunately parts of the sintered core broke off during the bronze pour and the broken core remnants can be seen as a rough surface embedded in the cast bronze at the base of the torso.

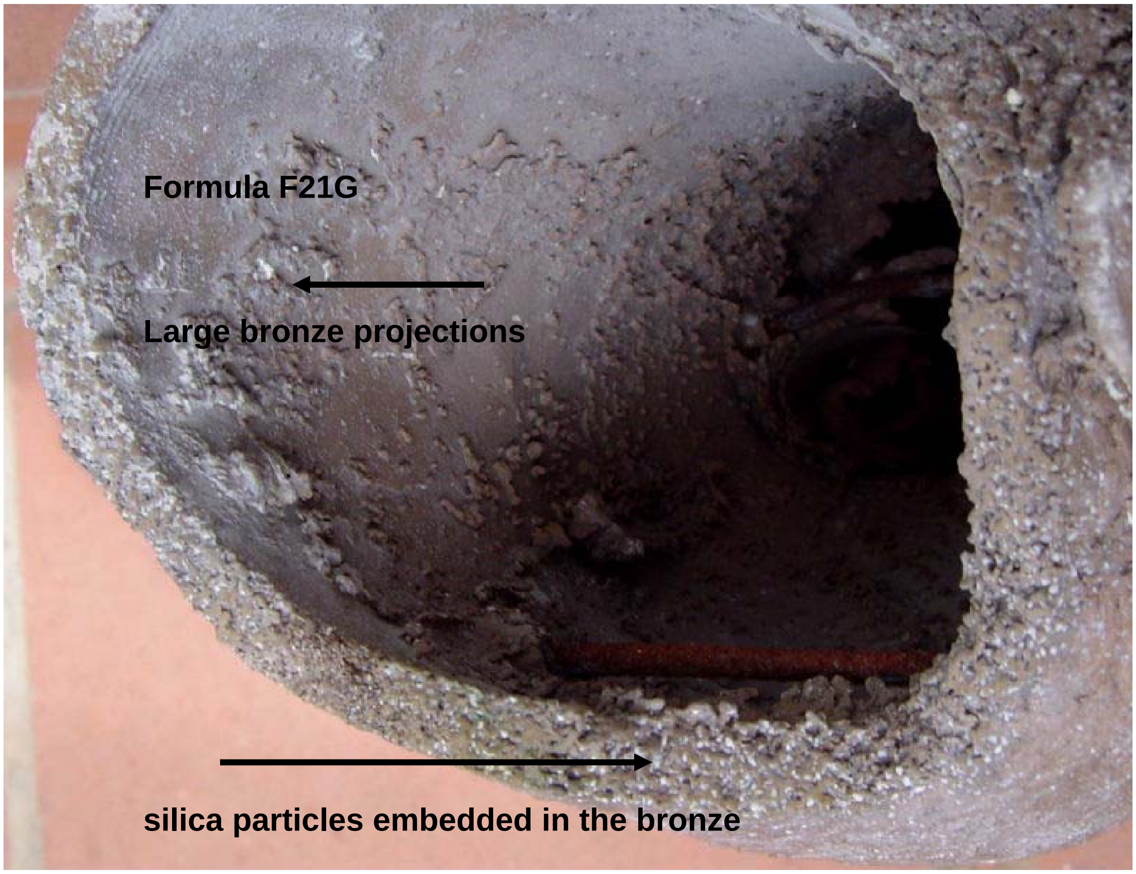


Figure 6.15 Another view of the base of the bronze female torso in which core formula F21G was used.

Note the particles of core that had broken off and embedded themselves in the base of the bronze mould. The inner surface is also marred not only with the bronze projections caused by air pockets in the wet mix at the time of pouring, but by larger projections of bronze caused by the break-down of the core. This experiment indicated that core formula F21G was too weak or fragile (or did not have enough binding power) to be used with any great success as a core in the bronze casting process.

Figure 6.16 A photograph of the outer surface of the female torso (300 mm high) cast in bronze using formula F21G as the core body.

The cast was poured from the top in this instance as can be seen from the attached pouring cup.

6.6.2 Observations

Once again, this time it was formula F21G that failed to meet the expectations of a good core formula, and although it could be easily removed from the cast bronze, it proved to be too fragile for practical purposes as some sections of the core broke off and were found embedded in the bronze at the base of the cast (cf. figure 6.15).

Due to this fact, it was decided to select a test formula that lay between F21A and F21G. In this regard, formula F21D was chosen and subjected to three bronze tests described in experiment 5 below, again using the female torsos as models.
Although it had already been established that a temperature of 945^{0}C would suffice, it was decided to double check the impact of the various sintering temperatures on the new formula (i.e. F21D).

Formula F21D used as the core mix in the three models would be sintered to 900^{0}C, 945^{0}C and 1000^{0}C (cf. sub-problem 4) to ascertain the disintegrating results (if any) that would manifest themselves at these three temperatures. At this time, these cores would not be subjected to relative humidity tests in the R H C apparatuses, but would be dislodged and removed from the bronze casts immediately the cores had cooled to room temperature (cf. 6.5.5 where cores could be dislodged from the cast bronzes as soon as they had cooled to room temperature).

6.7 Experiment 5 To evaluate the disintegrating characteristics of formula F21D when used as a core-body in bronze casting three hollow wax female torso models.

6.7.1 Discussion for experiment 5

The evaluation of formula F21D took the form of testing the core at three different firing temperatures, namely 900^{0}C, 945^{0}C and 1000^{0}C using three wax hollow female torsos as models. At this stage of experimentation the parameters that were deduced from core formulae F21 and F21G which produced either a difficult core to dislodge (F21, experiment 1) or a core that was very easily dislodged (F21G, experiment 4), were to be the guiding principal for the evaluation of formula F21D which was the next formula chosen to be tested as it had a silica composition that lay mid-way between the difficult to dislodge formula F21 (cf. table 6.1) and the easy to dislodge formula F21G.

6.7.2 Methods

The methods detailed in experiment 4 (paragraph 6.6) were followed here in coring, investing and bronze casting the three female torso models. As before, a thermocouple was inserted into one of the vent holes (15 mm in diameter) made in the core of each of the three female torso models under investigation. When the temperature inside the core (read by the thermocouple inserted into the cores) had reached the desired temperature within the core (which took approximately half an hour of soaking in the kiln in each case) the kiln was switched off.

Figure 6.17 A photograph of a bottom view of the inverted female torso mould illustrating the placement of the thermocouple in one of the vent holes made in the core soon after the core was poured.

The temperature inside the kiln and the temperature inside the core for each mould was monitored during the sintering process and the kiln was soaked until the core interior reached the prescribed temperature. This soaking period lasted for approximately thirty minutes in each case.

The bronze was poured into each of the three moulds at approximately 1200^0C and was allowed to cool naturally, which took approximately six hours. It is again noted that in this particular core formula, the bronze cannot be cooled by plunging the hot mould into cold water as this process will only cause the core to “set” as the plaster of paris in the formula re-hydrates (cf. sub-problem 3, summary 4.7).

Once the cores had reached room temperature, a long screwdriver was used to dislodge each of the cores previously fired to 900^{0}C, 945^{0}C or 1000^{0}C. This process took a maximum of ten minutes in each case, after which only remnants of the core remained. These remnants were easily cleaned away using a sandblasting machine set at six bars pressure and with a shot of 0,2 – 0,7 mm.

Figure 6.18 The three bronze female torsos (300 mm tall) whose cores were fired to 900^{0}C, 945^{0}C and 1000^{0}C.

6.7.3 Observations

It had already been established that the core formulae in the naked test bars became weaker as the sintering temperature was raised (cf. tables 5.1 and 5.2). It was assumed that the core removal for the core sintered to 1000^{0}C would be more easily done than the core fired to the lower temperatures of either 900^{0}C or 945^{0}C. However, there appeared to no difference in the degree of difficulty in dislodging the differently fired cores from the hollow bronzes, and if there was a difference, it was very minor indeed.

For this reason it was decided to conduct future core experiments to a firing temperature of 900^0C.

Although experiment 5 (with formula F21D) showed all the attributes of a good disintegrating core-body, it was decided to further investigate the next formula in the series F21 to F21G, being F21E. This formula should theoretically be more easily removed from a narrow wax tube (300 mm x 30 mm), the female torso model or from a larger four-litre open-ended mask model than F21D due to the increase in the silica content in its formula,

6.8 Experiment 6 To evaluate the disintegrating characteristics of formula F21E fired to 900^0C in a bronze casting scenario.

6.8.1 Discussion for experiment 6

In experiment 5, paragraph 6.7, it was determined that a firing temperature of 900^0C would be accepted as the firing temperature of choice, as it was established that the higher firing temperatures of 945^0C and 1000^0C made no apparent difference to the degree in which the core F21D could be removed from the bronze cast (cf. observation 6.7.3). At 900^0C, the outer ceramic shell is sintered to a hard enough degree to withstand the bronze cast in the various sizes used in the small art bronze foundry, as has been determined by the practical experience and confirmed in discussion with D. Jones, the resident lecturer at the PET studio foundry. It should be noted that the higher the sintering temperature, the more robust the ceramic shell becomes which in turn makes it more difficult to remove from intricate bronze surface detail. It is thus an advantage to sinter the ceramic shell preferably to 900^0C rather than to the higher temperatures approaching 1000^0C.

Three different wax models would be used to determine the disintegrating parameters of formula F21E, these being a long narrow wax tube 300 mm x 30 mm, the thirty-one centimeter tall female torso and a larger four-litre open-ended wax container. The long narrow tube was to verify the ease with which the core can be removed from the interior of a difficult to reach cast, the female torso was to verify the ease of removal for a general type cast and the open-ended four-litre wax container was to test the core to its limits in a vessel with a large volume versus the narrow confines of the tube and the normality of the female torso (cf. delimitations 1.6.13).

6.8.2 Method

The formula F21E (cement 2 parts, calcium carbonate 2 parts, plaster of paris I part and silica (0,95 mm) 7 parts) was mixed with 3 parts by volume of de-ionized water to produce a pourable mass. The mixture was poured into the respective moulds and shaken to ensure that the mix settled against the inner wax of the model (hopefully with as few as possible air pockets being created) to ensure that a smooth bronze cast finish to the interior of the cast is achieved. If the mix is too dry, then shaking the core inside the hollow wax prior to it setting, is not sufficient to achieving a smooth inner cast as the mixture with its high silica content leaves air pockets on the inner wall surface. The wax moulds containing the poured cores were left to set for six hours before they were invested in the ceramic shell. After seven days the models were de-waxed and were cast in bronze (cf. method described in experiment 5 paragraph 6.7.2).

6.8.3 Observations

The bronze surface results obtained in all three models (the wax tube, the female torso and the open-ended four-litre container), when using formula F21E, indicated these were not as satisfactory as the results obtained for formula F21D (cf. experiment 5). The following photographs will be used as a way of explanation, to illustrate the defects that occurred in formula F21E, as is indicated in the figures to follow (Figure 6.19 – 6.23)

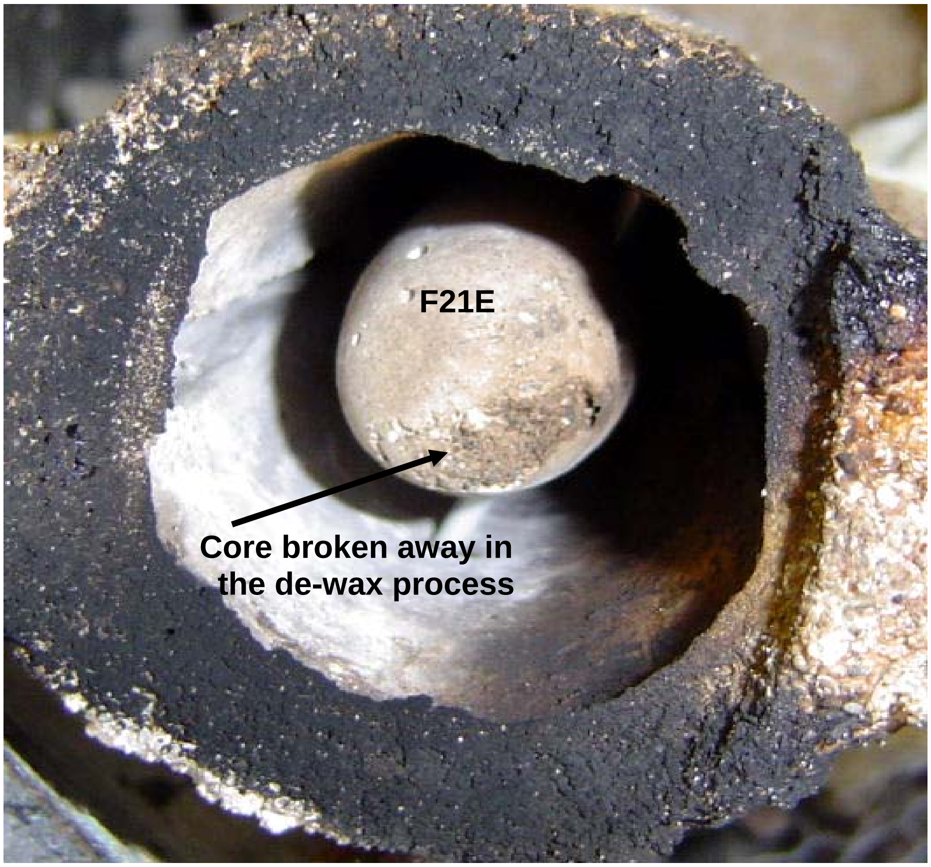


Figure 6.19 A photograph illustrates a cross-section of the bottom view of a mould where the wax from a narrow wax tube (300 mm x 30 mm) has been melted out in the de-wax process, exposing core F21E (centre of photograph) still attached to the outer ceramic mould by galvanized roof nails.

It can be observed that the core in the center of the photograph has broken away on one side during the de-waxing process; illustrating that core F21E is not as robust or as satisfactory as core formula F21D. This breaking down of the core formula F21E is again illustrated below.

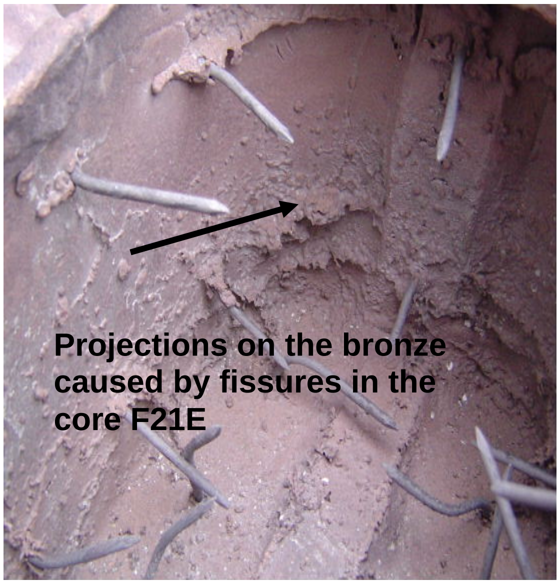


Figure 6.20 core formula F21E removed.

Figure 6.21 core formula F21E removed.

Figure 6.20 presents a view of the bottom section of the female torso cast in bronze, with core F21E removed. It will be noticed that the long bronze projections inside the torso indicate that the core fissured at this point, which most likely occurred either during the de-waxing process or during the bronze pour. Figure 6.21 is a view inside the larger bronze open-ended four litre container, with the core F21E removed, but with the core pins still in position. The protrusions attached to the bronze in figure 6.21, again illustrate that the core must have either broken down by fissuring in the de-waxing process or in the actual bronze pour.

Formula F21E, although it proved to be a fairly successful and usable formula when cored in the three model variants of a long narrow tube, a female torso and the open-ended four litre container, as illustrated in the three photographs (figures 6.19, 6.20 and 6.21) did however show signs of having less binding power than formula F21D when its fired surface was scraped open using a sharp pointed knife.

Figure 6.22 A photograph of the compacted surface of fired core formula F21E.

In the top half of the photograph, the surface of the core has been scraped away to reveal the underlying disintegrated core mass composed of powder and silica particles. Note the air pockets in the core surface in the lower half of the photograph. These air pockets reveal themselves as protrusions in the cast bronze (cf. figure 6.20) where this phenomenon can be seen as small lumps on the bronze in upper half of the female torso bronze mould.

The compact surface of the core as illustrated in the photograph above acts as a kind of barrier to the underlying mass and to the molten bronze during the bronze pour, preventing the molten bronze from scouring out the silica particles that lie just below this compact surface. (cf. previous observation in experiment 3, paragraph 6.5.3, figure 6.11).

The compact surface of the core is a natural occurrence where the finer materials in the wet mix are observed to segregate to the mould surfaces when the mix is agitated. This surface effect occurs when the naked test bars are made in the silicone rubber mould or in the cores made in wax moulds i.e. long narrow tubes, the female torso or the mask moulds.

The following two photographs illustrate bronze casts of the female torso with either formula F21E or F21D used as the core.

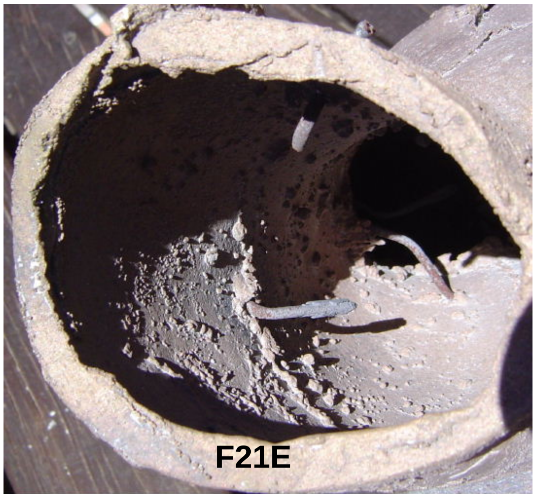


Figure 6.23 Bronze cast with F21E.

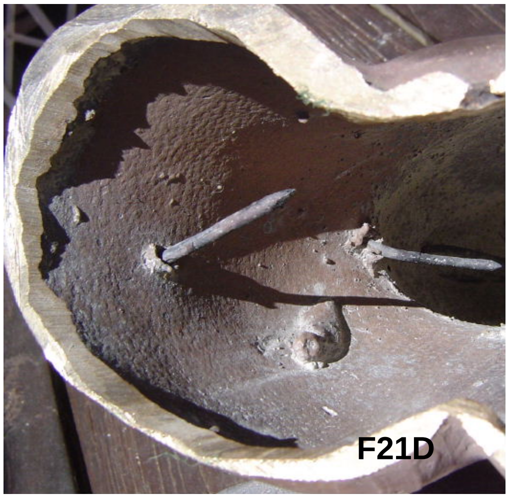


Figure 6.24 Bronze cast with F21D.

6.8.4 Summary

The comparison between the results obtained from core formula F21E in figure 6.23 and core formula F21D in figure 6.24 highlight the differences in these two core formulae. The raised protrusions in figure 6.23 were the result of air pockets in the core mix which can also occur in formula F21D (cf. figure 6.30) if it has not been sufficiently wetted with de-ionized water. It is the fissuring that occurs in core F21E that differentiates the two formulae (cf. figures 6.23 and 6.24). Formula F21E is only partially satisfactory whilst formula F21D has proved itself to be superior in all respects as a disintegrating core-body (cf. 1.1.5 factors that need to be examined prior to the development of a disintegrating core-body).

Formula F21D indicated in the experiments conducted to this stage that it was a more successful formula than formula F21E. It was therefore decided to return to formula F21D in experiment 6.7.

Three further experiments would be conducted to further verify the adaptability of formula F21D as a core body. Three open-ended four-litre wax models which have more than twice the volume of the female torso models were selected for this final test. After coring and investing the models in the ceramic shell, the moulds were sintered to 900^0C and were then subjected to the bronze pour.

To further verify the reliability of the core formula under abnormal delayed conditions, one of the moulds would be poured in bronze soon after being sintered to 900^0C whilst the other two moulds would be poured after a delay of six hours.

6.9 Experiment 7 The re-evaluation and confirmation of the disintegrating characteristics of formula F21D when used as a core in three large open-ended four-litre wax models, invested in the ceramic shell and sintered to 900^0C.

6.9.1 Method

Three tests were conducted in this experiment. The first test was when bronze was poured into the mould as soon as possible after the core had been sintered to 900^0C and the second test was when the molten bronze was poured into the remaining two moulds after a period of six hours had elapsed using the two different wax moulds photographed in figures 6.27 and 6.28.

6.9.2 Observations

The first mask was cast within half an hour after it was taken from the sintering kiln. The remaining two masks were left in the sintering kiln that had been switched off when the first mask was removed for a further six hours prior to been poured in bronze. This experiment which included a time delay of six hours was conducted as a precaution to determine whether any unforeseen core degradation within this time interval occurred in the event of a mishap happening in the casting process which could not be rectified within a shorter space of time. All three moulds cast immediately and after a delay of six hours proved to be successful in all respects.

Core formula F21D proved without doubt to be a successful core-body not only in long narrow models but also in general type one and a half litre models as well as in larger open-ended four-litre models. The core-body was more easily removed from the large open-ended models as compared with the long narrow tube shapes, but in all cases the core was easily removed and only required a brief period of sandblasting to free the last remnants of the core. The core did not break down in any of the models tested as was in the case in formulae F21E and F21G.

The photograph 6.25, illustrates the open-ended mask (with a volume of four litres) that was used as a model in the test to verify the performance of formula F21D which was cast in bronze soon after being fired to 900^0C. The bronze cast has only been partially cleaned at this stage to illustrate the core removal process.

Figure 6.25 A photograph of an open-ended four-litre mould illustrating how crumbly the core (formula F21D) had become once it had been gouged with the screwdriver.

The core was removed within ten minutes illustrating the ease with which it could be removed from bronze casts.

Figure 6.26 A photograph of the open-ended four-litre mask with the outside ceramic investment partially removed.

This photograph indicates that the core (formula F21D) came away readily before the bronze cast was subjected to the sandblasting procedure where the final remnants of the ceramic shell are removed.

Figure 6.27 Four-litre mask.

Figure 6.28 Four-litre mask

Figure 6.29 Internal view of figure 6.27

Figure 6.30 Internal view of figure 6.28

Figures 6.29 relates to its counterpart, the open-ended face mask figure 6.27 and figure 6.30 relates to its counterpart, the open-ended face mask figure 6.28. The photograph on the left (figure 6.29) illustrates the result obtained when the core mix (F21D) was correctly wetted with 2,9 parts by volume of water and was thus easily poured into the wax mould resulting in a core with no apparent air pockets. The photograph on the right (figure 6.30) illustrates by way of example, the characteristic effect obtained when the core mix was not sufficiently wetted with the enough water (2,5 parts by volume in this instance) with the subsequent result of introducing air pockets into the drier mix and thus creating air pockets against the inner surface of the wax mould. These air pockets in turn transform themselves into projections on the bronze surface illustrated in figure 6.30.

6.9.2 Integrity of the outer surface of the bronze cast

All the outer surfaces of the bronze casts facing the ceramic shell investment were unmarred due to formula F21D not breaking down during the bronze pour, thus ensuring that the integrity of all the outer surfaces of the bronze casts were maintained at all times.

6.9.3 Volume and parts by weight measurements

In the delimitations to this investigation (cf.1.6.8), it was originally decided that a parts per volume method would be used in all core formulae measurements. It was further stated that when a final formula had been developed, this formula would be tabled in parts per volume as well as in parts per mass, so that future investigators could use either method in their investigations and in the suggestions for further research as outlined in chapter seven.

Formula F21D	Parts by volume	Parts by weight	Percentages by weight
Cement	2	11,0	14,8%
Calcium carbonate	2	9,2	12,4%
Plaster of paris	1	3,3	4,4%
Silica 0,95 mm	6	39,1	52,6%
De-ionized water	2,9	11,6	15,6%

Table 6.5 A conversion table for converting parts per volume to parts by weight for formula F21D.

6.9.4 Summary

From the results of the experiments conducted in chapter six, formula F21D was selected to be the formula of choice as a core-body suitable for a wide range of hollow bronze casts (cf. def of terms 1.10.7). It proved to be better than formula F21, which was too robust and difficult to remove from the bronze casts and superior to both formulae F21G and F21E which proved to be too fragile as indicated in experiments 4 and 6 respectively.

Formula F21D can be used as a core-body in making hollow cast ware with small narrow apertures as described in the hollow wax tubes with the dimensions of 300 mm x 30 mm (200 ml) to statuette type moulds represented by the female torso which is 300 mm high (1.5 litres) to the large open-ended mask type hollow casts with a capacity of four litres. It should be noted once again that the open-ended hollow four-litre mask type moulds are at the extreme limit for this type of core-body as they begin to become too heavy and cumbersome for practical use in a small art bronze foundry and other methods should be employed where the cast is cut into smaller sections, invested in the ceramic shell, cast in bronze and the sections welded together to form the complete bronze cast.

Core formula F21D fired to a temperature of 900^0C was found to be the most acceptable core-body that fulfilled the parameters set out in the statement to the problem, for the development of a disintegrating core-body for use in the ceramic shell bronze casting process.

CHAPTER 7

CONCLUSION

7.1 The problem

What is the optimum formula for a quick-setting core-body, which is wholly suitable for a wide range of hollow bronze casting activities within the small art foundry context and which will also disintegrate within a specified period of time thus obviating tedious mechanical assistance and/or the use of chemical agents for its removal?

A major challenge in this study has been to relate objectively to a core body that can be correlated to performance and reliability under investigation.

It was therefore essential to relate to both quantitative and qualitative changes in core disintegration that bore a relationship to the different properties and performance behavior of the core body and alternatively to the integrity of the cast bronze piece.

The limitations of this study involved using four principal types of refractory materials, namely, cement, plaster of paris, silica and calcium carbonate in a specific combination derived by empirical experimentation. Although the material choice was not exhaustive, it nevertheless gave reliable and repeatable results when the firing and relative humidity conditions were within specified limits (cf. delimitations 1.6.12).

The study began with an investigation of the properties of cement, plaster of paris, silica and calcium carbonate as well as calcium hydroxide (cf. sub-problem two) and hence determining their contribution, singly and in combination to produce an acceptable core formula.

A brief overview of the findings addressing the five sub-problems, which were related to the development of a disintegrating core formula, for use in conjunction with the ceramic shell investment process as used in bronze casting process follows hereunder.

7.2 The first sub-problem

What materials or combination of materials can be used to produce a quick-setting core formula for use in the ceramic shell process that will disintegrate within 72 hours, under controlled conditions of temperature and relative humidity?

The tests undertaken for sub-problem one (as indicated in chapter two) produced clear indications as to the relationships between cement, plaster of paris, silica and calcium carbonate and the disintegrating characteristics of these various combinations under particular temperatures and relative humidity conditions.

Seventeen formulae were investigated, including pure cement and plaster of paris, a combination of cement and plaster of paris as well as various combinations of cement and silica or plaster of paris and silica or cement and calcium carbonate or plaster of paris and calcium carbonate. The combination of cement, plaster of paris and silica as well as the combinations of cement, plaster of paris and calcium carbonate and silica were also tested (cf. table 2.2).

The factors pertaining to the methodology that were pertinent to the sub-problem one are discussed below:

Choice of materials (cf. methodology 1.5.7)

The choice of the core materials was limited to four ingredients, namely, cement, plaster of paris, silica and calcium carbonate with the inclusion of calcium hydroxide conducted in the experiments in sub-problem two, 3.4 (cf. methodology 1.5.7).

It was suspected that the four ingredients would contribute individually and in combination to the disintegration of a core-body and is summarized as follows:

- Cement: setting and spalling agent.

- Calcium carbonate: disintegrating agent.

- Plaster of paris: rapid setting and binding agent.

- Silica: a particulate disintegrating agent acting in combination with the spalling effect of cement (cf. def. of terms 1.10.5) and the disintegrating contribution by calcium carbonate (cf. literature review 1.4.10).

Cement proved to be satisfactory (cf. literature review 1.4.4) as a refractory material to molten bronze at 1200^0C, with spalling characteristics (F2), which were altered by the introduction of materials such as calcium carbonate (cf. formula F11). The spalling characteristics of cement in conjunction with calcium carbonate are the two main ingredients in the formula that allowed the fired mixture to disintegrate. It must be noted that in the choice of Portland cement, CEM 11/ A-L 32,5 Portland limestone cement produced in Port Elizabeth that other cements produced with different specifications could have been used. However, it was initially decided to use only one grade of cement as the permutations would become too great if different varieties of cement were used and this would then result in a body of work outside the scope of this thesis (cf. delimitations 1.6.14.2).

Calcium carbonate provided enhanced disintegrating properties to the compound formula mixes, by converting to calcium oxide when heated to above 900^0C, as well as providing an assumed porosity to the core as it was converted from calcium carbonate to calcium oxide with a weight loss of 43% (cf. literature review 1.4.10).

Plaster of paris proved to be beneficial as a quick setting and binding agent in the compound core mixes and in combination with these formulae mixes it did not sinter to form a hard mix when subjected to temperatures of between 900^0C and 1000^0C (cf. formula F1, table 2.1).

The inclusion of silica in the formulations helped to reduce the shrinkage rate of the formulae and it was found that silica (0,95 mm) through experimentation provided the best results in the disintegrating core, (as compared to silica 200 mesh and silica 0,2 mm) not only for its expanding and contracting characteristics at 573^0C, but also due to the rounder shapes of the particles which provided a core body that could not compact to the same degree as with the stiletto or angular type and smaller particle sizes of silica 0,2 mm or to a greater extent with silica 200 mesh (cf. methodology figure1.2 and figure1.3).

The sequence of formulae tests (cf. methodology 1.5.4)

The sequential pathway for the preliminary development of a disintegrating core formula proved to be successful, after the initial parameters for the materials had been established in steps1 to step 6, as detailed in chapter 2.

Empirical testing methods (cf. methodology 1.5.5)

As previously outlined in the delimitations (cf. delimitations 1.6.9 empirical testing) a minimum of three tests would be repeated for each experiment. Three repeat tests in each of the experiments were deemed to be sufficient as the results from these tests were intended as directional indicators only, which in turn would lead to the next step in the sequence that was to be taken in this investigation.

Volume measurements (cf. methodology 1.5.6)

The method of using volumes (parts by volume) in the formulae testing was used to produce formulae that would indicate trends and pathways for the following set of formulae experiments in the investigative process. It is noted that the parts by volume method is not a very accurate method to use, but if it is used in a consistent manner in conjunction with the same batches of ingredients, then this method of measurement for use in the art studio bronze foundry environment should prove to produce formulae that are consistently uniform and reliable.

Shrinkage tests (cf. methodology 1.5.11)

The naked test bars moulded in the silicone rubber mould proved to be successful. The shrinkage tests could thus be repeated six times for each formula mix in order to verify the shrinkage values of the different formulae tested in the experiments.

The R H C apparatus (cf. methodology 1.5.13)

The three R H C apparatuses used to observe the relative humidity values within certain ambient room temperatures (fully described in the definition of terms 1.10.6) had serious shortcomings in that only general conditions of relative humidity could be recorded that in turn were dependent upon the ambient temperatures and the water vapour content prevailing in the room in which the R H C apparatuses were kept. However, these conditions measured inside the R H C apparatuses would later prove to be a source of investigative interest only that pertained to the early testing procedures on the naked test bars and which would later be set aside by default in the final formulae scenarios used for the cores in the actual bronze pours (cf. discussion in the foreword 6.6 sub-problem 5).

Selected firing temperatures for the naked test bars experiments (cf. methodology 1.5.12)

The three temperatures for the naked test bar experiments as well as the bronze core experiments in chapter 6 were exposed to temperatures of 900^0C, 945^0C and 1000^0C. These three temperatures gave definite indications as to how the naked test bars as well as the cores within the cast bronzes behaved at these three temperature variables. It was only in the final stages of development of formula F21D in chapter 6, that a single sintering temperature of 900^0C was finally chosen as a suitable consideration for the successful disintegration and removal of the core from the hollow bronze cast.

De-ionized water (cf. methodology 1.5.7.9)

The choice of using de-ionized water throughout this investigation was deemed necessary if the experiments are to be conducted at some future date in another locality.

Municipal water, bore-hole water and other sources, for example, water with a high salt content could affect the results obtained in these experiments and could be a source for further research.

Silicone rubber mould (cf. methodology 1.5.8)

The size of the seven individual moulds in the silicone rubber master mould proved to be a successful method of making a sufficient number of individual naked test bars, as they were large enough to show the changes that took place once the bars had been fired to various temperatures and then subjected to various relative humidity conditions as well as in the compression tests using the Hounsfield apparatus.

Summary statement

In answer to the question as to whether a quick-setting core formula could be found that would disintegrate within 72 hours under controlled conditions of relative humidity was only partly answered in the preliminary development of formula F17. It required further testing and modifying in the following four sub-problems before this question would be satisfactorily resolved as a final working core formula.

In the experiments conducted in chapter 2, the formulae 16 and 17 both broke down (disintegrated) within 72 hours and 60 hours respectively. However the shrinkage values of these formulae were too, high being between 1,6% -1,7% and 1,7% respectively. This indicated that further experimentation was still necessary to develop a formula that would disintegrate within 48 hours, yet have shrinkage values equal to or below 1%.

Both formulae F16 and F17 set to a firm mass within six hours of pouring as compared with pure cement at 12 hours and plaster of paris at 4 hours indicating that a formula could be made with quick-setting properties.

7.3 Second sub-problem

What is the most effective formula that can be developed from the most promising formulae investigated in the first sub-problem, which will ensure that the core-body with quick-setting characteristics will disintegrate within 48 hours after firing and still have a shrinkage value of equal to or less than 1%?

In addressing the tests undertaken for this sub-problem (as indicated in chapter 3) produced clear indications that by altering the formulae containing the four selected ingredients, namely, cement, plaster of paris, silica and calcium carbonate, a formula could be determined that would disintegrate within 48 hours and have a shrinkage value equal to or less than 1%, namely formulae F22, F23 and F24.

It was discovered in the experiment that by increasing the quantity of silica (0,95 mm) in the core formulae, (cf. table 3.3), that the shrinkage values could be progressively reduced to below 1% in the fired naked test bars (cf. table 3.3). However, as the shrinkage values decreased so did the apparent strengths of the fired naked test bars.

Calcium hydroxide was experimented with as an alternative to calcium carbonate at this stage of the investigation. However it was decided that calcium carbonate was superior to the action of calcium hydroxide in the context of the compound mix, due to the harder disintegrated mass that resulted when using calcium hydroxide. Formula F25 produced satisfactory disintegrating results and was included in the formulae carried forward to sub-problem 5 for further investigation.

The choice was therefore to leave out formulae F23 and F24 to keep the investigation with as few ingredients as was deemed necessary. It was therefore decided to compare formulae F21, F22 and F25 in sub-problem 5 under different relative humidity conditions.

The factors pertaining to the methodology that were pertinent to sub-problem two are discussed below.

Ambient temperatures (cf. methodology 1.5.12.2)

The ambient temperatures that were recorded during the relative humidity testing procedures were subject to the variable temperatures prevailing in Port Elizabeth at the time of the tests. These tests were not controlled by a constant temperature control apparatus, but were dependent upon the temperatures recorded in the designated room in which the R H C apparatuses were kept (cf. def. of terms 1.10.6). It was decided at the time of setting up the experiment that sophisticated instruments and apparatus outside the general availability to an art bronze studio foundry would be avoided and rather simulations close to those that could be copied by an art bronze studio would be used (cf. delimitations 1.6).

The results that were obtained at the different relative humidity values indicated that the disintegration of the naked test bar formulae was related to the degree of relative humidity in the air.

Summary statement

In answer to the question as to what the most effective core formula would be which would ensure that the naked core with a quick-setting characteristics would disintegrate within 48 hours after sintering and still have a shrinkage value of equal to or less than 1%, was only partly answered in that further experimentation would be necessary in the forthcoming sub-problems.

The reader is reminded that the reference to 48 hours as a time objective (cf. background to the problem 1.1.5) and to 1% as a shrinkage objective (cf. background to the problem 1.1.5), of the fired naked test bar were discussed in chapter 1 as being acceptable limits for a core used in the context of a small art bronze foundry.

7.4 Third sub-problem

What are the relative humidity considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal studio bronze casting procedures?

The tests undertaken for this sub-problem (as indicated in chapter 4) produced clear indications that there was a general relationship between the degree of relative humidity and the disintegration times of the core formulae.

The relative humidity tests for this series of experiments were of a general nature in that a relative humidity of a high, moderate and medium range were arbitrarily chosen (cf. delimitations 1.6.12). It was found that the relative humidity definitely played a part in the disintegrating times of the sintered naked test cores. In table 4.1, it was recorded that as the relative humidity was increased from 74% to 81% and then to 91%, so the disintegrating times for specific sintered test bars were progressively decreased.

The relative humidity of 91% at a general ambient room temperature close to 20^0C appeared to provide a good working environment for core formula F21 allowing it to disintegrate within 48 hours. The reader is reminded that in excessively damp conditions, for example if the fired core is sprayed with a fine mist of water, the core will not disintegrate but will instead form a core body that is robust and will not disintegrate, perhaps due to the plaster of paris in the formula becoming hydrated once again.

The factors pertaining to the methodology that were pertinent in sub-problem three are discussed below.

Relative humidity (cf. methodology 1.5.13)

The parameters for relative humidity testing procedures were limited to three ranges of temperature, namely, high, moderate and a medium relative humidity (91%, a propos 80% and a propos 74%). It must be remembered that the original nature of the investigation was to provide as practical a method as possible within the scope of the small art bronze caster (cf. introduction to the delimitations 1.6). These relative humidity values could have been further investigated but as the condition of relative humidity would be discarded by default in the final sub-problem five, this was not to be the case.

Summary statement

In answer to the question as to whether relative humidity influences the disintegrating characteristics of a quick-setting naked core formula, the answer is that the relative humidity does influence the disintegrating rate in such a way that as the relative humidity is increased so the disintegrating rate of the naked core-body in the form of sintered naked test bars increased.

7.5 Fourth sub-problem

What are the temperature considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal ceramic shell sintering parameters?

The tests undertaken in this sub-problem (indicated in chapter 5) produced three clear indications of how the naked test bars were affected with an increase in fired temperature, namely:

- Firstly, there was a small reduction in the shrinkage values as the temperature was increased.
- Secondly, the disintegrating times for the naked test bars were reduced at higher relative humidity values.
- Thirdly, the disintegration times for the naked test bars were reduced as the temperature was increased.

The factors pertaining to the methodology that were pertinent in sub-problem four are discussed below.

Firing temperature considerations (cf. methodology 1.5.18.2)

- The three temperatures (900^0C, 945^0C and 1000^0C) to which the naked test bars were subjected to, was restricted to the constraints of the sintering parameters of the ceramic shell being 900^0C to 1000^0C (cf. methodology 1.5.11.2).

- The temperature difference between 900^0C and 1000^0C only had a small effect of 0,1% on the shrinkage value as the temperature was increased from 900^0C to 945^0C and 1000^0C on the naked test bars which were used in the tests.

- In the case of the naked test bars it was found (cf. table 5.1 and 5.2) that as the firing temperature was increased so the disintegrating time was reduced.

- The effect of relative humidity on the disintegrating times was determined by exposing the fired naked test bars fired to 900^0C to 945^0C and 1000^0C, to a relative humidity of either 81% or 91%. It was found that at the higher relative humidity the naked test bars disintegrated in a shorter time period than at a lower 81% relative humidity.

Summary statement

In answer to the question as to what are the fired temperature considerations that will facilitate the disintegrating characteristics of a quick-setting core-body within the constraints of normal ceramic shell sintering parameters, the following were found:

- It was revealed that as the naked test bars were fired to 900^0C, 945^0C and 1000^0C, so the shrinkage values of the naked test bars decreased fractionally.

- Increased relative humidity (81% to 91%) decreased the disintegration times of the fired naked test bars at 900^0C to 945^0C and 1000^0C respectively.

- The naked test bar disintegrated more quickly (at similar relative humidity values) as the firing temperature was raised from 900^0C to 945^0C and 1000^0C;

These three temperature variants would be further investigated in experiments conducted in the fifth sub-problem to confirm or refute their usefulness as determining factors in the removal of the core from cast bronzes.

7.5 Fifth sub-problem

Would the conclusions inferred in the first four sub-problems be applicable to core formula/formulae when used for the actual production of a wide range of hollow bronze casts?

In addressing the fifth sub-problem, an initial series of empirical tests were conducted using the formula F21 as a core confined within a wide range of bronze casts (versus the unconfined naked test bars used in sub-problems 1, 2, 3 and 4). The results were that although the core disintegrated as expected, it was difficult to remove from the hollow bronze casts.

Formula F21 was subsequently modified, to determine whether by only increasing the silica content in the formula, the core could be more readily removed from the hollow bronze cast.

It was found that by increasing the content of silica (0,95 mm) from two parts per volume in formula F21 to nine parts per volume in formula F21G, that the disintegrated core material could then be more easily removed from the bronze casts. The increase in the silica content did not affect the disintegrating times but merely made the disintegrated core material easier to dislodge from the confines of a narrow bronze casts. Unfortunately formula F21G broke down to some degree in the actual bronze casting tests.

The evidence presented, proved that for the range of formulae from F21 to F21G that F21D had the best overall desired characteristics and more accurately fulfilled the brief of this research project. Even so it was decided to push the envelope by testing formula F21E to compare it with formula F21D for the sake of objectivity and thoroughness.

Formula F21E as expected proved to be more easily removed from a bronze cast than F21D, except for the fact that fissure-like projections appeared on the inside facings of the hollow bronze casts, indicating that it would be more prudent to revert back to F21D as a "safer" core for use in general casting conditions.

Formula F21D has a low shrinkage value and is not eroded by molten bronze. It is also very easily removed from the hollow bronze casts using a gouging tool or by sandblasting at six bars pressure with a shot with the approximate size of 0,2 – 0,7 mm.

The factors pertaining to the methodology that were pertinent in sub-problem 5, are discussed below.

The wax test moulds for use in experimental bronze pours (cf. methodology 1.5.16)

Firstly, the wax tubes with the dimensions of 300 mm x 30 mm, were deemed to be necessary in order to identify the positive and negative characteristics of the core formulae F21, F21A, F21B, F21C, F21D, F21E, F21F and F21G, and to further identify and thereby be able to choose a formula that would comply with the parameters specified in the background to the problem (cf. 1.1.4 and 1.1.5).

Secondly, the wax moulds in the form of the female torso were also necessary to verify the characteristics of the formulae under investigation when used with models larger in volumes.

Thirdly, in the final set of experiments using formula F21D to assess the characteristics of a large volume mould of four litres capacity it proved to be successful.

This series of tests also identified that formula F21D could be used within a period of six hours after being fired in the ceramic shell to 900^0C to the time of pouring the bronze, as a precautionary measure in times when the bronze could not be poured close to the time that the core reached its sintering temperature (cf. experiment 6.7).

Relative humidity

In experiment 6.4 the effects of relative humidity proved to be of no real consequence in removing the core formulae F21 to F21G from bronze casts, as the cores could be quickly removed from the bronze casts as soon as they had reached room temperature. This fact of not having to wait a certain period of time to be able to remove the core from the cast proved to be a positive benefit for the core formula when used in a bronze casting scenario.

Compression breaking strength determinations (cf. methodology 1.5.10)

It was found that compression experiments (using the Hounsfield apparatus), for the naked test bars would only indicate in general terms what the strength of the various fired naked test bars was due to the fact that the naked test bars were not perfectly homogenous. The three materials namely cement calcium carbonate and plaster of paris disintegrated to a dust and the silica remained unchanged. The compression results did however indicate that as the silica content (0,95 mm) was increased, so the strength of the sintered naked test bars decreased. This observation led to determining the final set of parameters for formula F21, and the modification thereof to formulae F21A, F21B, F21C, F21D, F21E, F21F and F21G in chapter 6.

Summary statement

Would the conclusions inferred in the first four sub-problems be applicable to core formula/formulae when used for the actual production of a wide range of hollow bronze casts?

In answer to the question as to whether the conclusions inferred in the first four sub-problems would be applicable to core formula/formulae when used in the bronze casting process is answered below in a the form of a review of the results obtained in the first four sub-problems as well as the results obtained in the fifth sub-problem:

- A disintegrating core-body was developed for use in the ceramic shell bronze casting process that disintegrated within 48 hours (cf. first and second sub-problems). In fact, by default, it was found that the core could be removed from the bronze cast as soon as the core had cooled to room temperature (cf. fifth sub-problem).

- The rate of disintegration of the fired naked test bars was observed to be dependent on relative humidity (cf. third sub-problem), but for the sake of expediency, the parameter fell away when it was discovered that the core could easily be removed as soon as it had reached room temperature (cf. fifth sub-problem) regardless of relative humidity.

- The increase in the rate of disintegration was dependent upon the naked test bars being sintered to 900^0C, 945^0C or 1000^0C (cf. forth sub-problem), but it was found that there was very little difference in the disintegration times of the cores used in bronze casts (cf. fifth sub-problem).

7.8 Hypotheses

The original hypotheses as stated in chapter 1 (cf. paragraph1.9), are repeated here and will be discussed below:

It is given, that a typical core (used in the art studio bronze casting process), will be made from a mix of materials that produce a core that has a minimum of shrinkage and is refractory to the molten bronze. Unfortunately these ideal core formulations do not lend themselves to easy removal from the hollow bronze cast models.

Within this specific context the hypotheses were originally formulated as follows:

7.8.1 First hypothesis

With the manipulation of certain materials or combination of materials, one will be able to initially produce a quick setting core formula that will disintegrate within 72 hours under controlled conditions of temperature and relative humidity.

The tests in chapter 2 produced clear indications that with the manipulation of the four chosen materials, namely, cement, plaster of paris, silica (0,95 mm) and calcium carbonate, one is able to formulate a quick-setting core-body that will disintegrate within 72 hours after having been fired to 945^0C.

The formulae F16 and F17 had quick-setting properties as well as disintegrating within 72 hours.

This confirms hypothesis 1.

7.8.2 Second hypothesis

An effective core formula can be produced by the manipulation of various selected refractory materials which will disintegrate within a specific period of time, namely 48 hours, and in addition will have a shrinkage value of equal to or less than 1%.

The tests in chapter 3 produced clear indications that a formula can be made using the four chosen materials to produce a core that disintegrates within 48 hours and has a shrinkage factor of equal to or less than 1%.

Formulae F22, F23 and F24 made from the four materials, namely, cement, plaster of paris, silica (0,95 mm) and calcium carbonate had a shrinkage factors of less than 1% and also disintegrated within 48 hours.

This confirms hypothesis 2.

7.8.3 Third hypothesis

The relative humidity will have a significant influence on the disintegration times of the formulated sintered core body.

The tests in chapter 4 produced clear indications that the degree of relative humidity in the atmosphere has a decided bearing on the rate at which the formulated core bodies disintegrate.

The higher the relative humidity (up to 91%), the more quickly the fired naked test bars disintegrated as indicated in table 4.1 and 4.2.

This confirms hypothesis 3.

7.8.4 Fourth hypothesis

The temperature to which the formulated core body is heated in the kiln will have a significant influence on the disintegration time and shrinkage rate of the formulated core-body.

The tests in chapter 5, produced clear indications that the temperature to which the core is heated, has a direct bearing on the disintegration times as well as on the disintegration times under different relative humidity conditions of the fired core.

Only small changes in the shrinkage values were recorded when the core formulae were subjected to the firing temperatures of between 900^0C and 1000^0C.

This confirms hypothesis 4.

7.8.5 Fifth hypothesis

That once the four sub-problems have been addressed, a disintegrating core formula can be developed that can be easily removed from a wide range of hollow cast bronzes by using either a gouging metal tool or a sandblasting machine.

The tests in chapter 6, produced clear indications that a core formula was developed that could be easily removed from the hollow cast bronze using either a metal gouging tool or a sand blasting machine set at six bars pressure with a shot of approximately 0,2 – 0,7 mm in size.

This confirms hypothesis 5.

7.9 Summation

The statement of the research problem

What is the optimum formula for a quick-setting core-body, which is wholly suitable for a wide range of hollow bronze casting activities within the small art foundry context and which will also disintegrate within a specified period of time thus obviating tedious mechanical assistance and/or the use of chemical agents for its removal?

The statement of the research problem can now be answered as follows:

- The creation of a refractory core formula, F21D, with the formula 2 parts cement, 2 parts calcium carbonate, 1 part plaster of paris, 6 parts silica (0,95 mm) and 2,9 parts of de-ionized water, has been successful developed.
- The investment process can commence within six hours after the core has been poured into a hollow wax cast.
- The core can be removed with a little mechanical assistance within a few minutes of the bronze cast cooling to room temperature.

7.10 Proposed recommendations to further research

The advantages and disadvantages of the core formula developed in this document are listed below and it is from these parameters that further experimental research will be advanced.

Delimitations of the core formula F21D

- The core due to its disintegrating nature must be used within six hours of the final sintering temperature having been attained. The time limits set for the core do not allow batches of moulds containing cores to be sintered and then kept for more than six hours to accommodate large production techniques as found in the larger foundries.

- The weight of the wet core, being two kilograms per litre, will limit the practical size of the moulds containing cores that can be cast. For larger casts than those described in the thesis, a core body containing lighter materials such as kieselguhr (diatomaceous earth) or aerated alumina may be chosen.

- The waiting period of seven days for the cement content of the core to cure, can be a disadvantage in cases where a bronze needs to be cast in a hurry. The ceramic shell process can be hurried along by force-drying the investment stages, in which case a mould can be made within three days. However the parameters set out for this study allowed a normal period of seven days from the time the core is poured to the time the bronze is poured, which is ultimately a better option than having to weld sections of a bronze cast together where a core is not used.

- The control of the kiln temperature and the monitoring of the internal temperature of the core can be burdensome, as compared with the wide tolerances that can be sustained by other core formulae.

- The hot cast bronze containing the core should not be plunged into cold water to anneal the bronze as is done at the PET, as the water will react with the core formula, re-hydrating the plaster of paris in the formula, which in turn will set into a hard mass making the core difficult to remove. This annealing of the bronze cast has advantages, for example, when bronze extensions like animal legs on the cast require to be bent into shape, but generally art bronze pieces do not require to be reworked to this degree after the casting.

Advantages of the core formula F21D

- The mixing method for the core formula is straightforward and does not require any special equipment.

- The ingredients are easily obtained from most building suppliers.

- The removal of the core does not require specialized tools or chemicals.

- The core can be removed using a rudimentary tool such as a long screwdriver or a more sophisticated method of using a sandblasting machine can be employed, which is generally standard equipment in most studio foundries.

- The core can be quickly removed as soon as it has reached room temperature, leaving a clean internal surface without any pieces of core attached to undercuts within the bronze mould.

- The pre-sintered mould can be stored in a clean environment for long periods of time without any deterioration in the core.

- The high weight of the wet core slurry is easily accommodated in small art bronzes as illustrated in the female torso and masks.

Proposed experimental parameters that could be advanced as recommendations for further research:

The following experimental proposals are not necessarily promised to be solutions, but offer possible alternative avenues for further research.

- To produce a lighter core mould, one might introduce kieselguhr (diatomaceous earth) into the formula (it being a light pourous siliceous material derived from sea diatoms).

- Introduce combustible materials such as a hard wood sawdust which does not absorb water to the same degree as a soft wood sawdust (which would prevent swelling in the initial mix when the core is poured into the mould) which by its very nature reduce the weight of the core.

- Introduce lightweight materials such as coal fired power station fly ash granules into the formula that would remain inert in the mix but would contribute to the binding power of the core mix. Fly ash can be used as a diluent or extender in cement mixes but here it is used in the form of a very fine powder to achieve the same particle size as bagged cement. Fly ash in different granular sizes would open a new avenue of research in that the fly ash may contribute to many new positive advantages to name a few such as the jiggered shape of the particles, the porosity of the particles, the refractory qualities, the light weight and the contributing factor to strength to the cement mix. The discussion on the merits of adding fly ash to a cement mix as well as the physical and chemical properties of South African fly ashes is discussed in detail in the thesis written by Grieve (cf. Grieve,1991).

- The time period of seven days for the core to cure inside the hollow wax model could be investigated. The object of this investigation would be to determine whether this time period could be reduced by either adding drying or setting agents to the formula or by curing the core under different atmospheric conditions.

- The development of a disintegrating core in this research was limited to CEMENT 11/ A-L 32.5 Portland limestone cement. The introduction of other types of cement will be recommended as a subject for further research.

GLOSSARY OF TERMS

Aggregate: formed by the collection of particles into a mass, example crushed stone in a cement mix.

Almod 70 plaster of paris: A branded plaster of paris made in Germany.

Bronze: Ammen, (1980:117) **"**Bronze is not a alloy of definite composition. It is an alloy of copper and tin. It may also contain small amounts of other elements…When tin is added to copper it increases its hardness and strength. Zinc is sometimes added in small amounts to improve the casing properties".

BPB Gypsum (Pty) Ltd, Cape Town. Plaster manufactures of BPB plaster of paris.

Bronze pouring temperature: Bronze is heated to 1200^0C and poured at between 1175^0C and 1150^0C.

C_3S: tri-calcium silicate

Casting: the act of pouring molten metal into a mould.

Cement paste: *Fulton's concrete technology*, 2001:11, Addis refers that: "Fresh paste consists of cement particles dispersed throughout water-filled space".

Ceramic shell investment: a combination of silica sol slurry and chamotte is applied in layers to build up a mould approximately 5 to 10 mm thick around a wax model that will be used in the bronze casting process.

Control-room: this is a designated room away from direct sunlight and having a door that closes to prevent draughts, which could upset the temperature and relative humidity readings recorded throughout the testing procedures.

Core formula: the core made from a specific refractory formula used in the lost wax casting process for hollow cast items.

Core pin: seven centimeter zinc clout nails are used as core pins as the zinc layer corrodes in the sintering process of the ceramic shell, which then allows them to be easily extracted from the cast bronzes.

Colloidal silica sol: A colloidal suspension of silica in an aqueous medium used in combination with certain fillers to make colloidal silica slurry used in the ceramic shell investment process.

Curing of cement: Curing is the process of ensuring that sufficient moisture is available for continued hydration. Curing should continue for at least 7 days after casting. Cement attains its maximum strength after curing in damp conditions for 28 days.

De-ionized water: a clear, colourless, odourless, and tasteless liquid prepared from suitable potable water by the treatment with ion-exchange materials.

Empirical testing criteria: a testing method that is derived from or depending upon experience or experiment alone.

R H C apparatus: an insulated box 400 mm x 400 mm x 400 mm, specially constructed for this thesis, which has a removable lid with a viewing window to observe the maximum and minimum thermometer as well as the relative humidity thermometer. There is place in the apparatus for a plastic trough with a metal grid placed over it for the test pieces to rest upon.

Kiln soaking period: this is usually the top temperature, which is maintained for a pre-set period of time. In this thesis a soak period of 30 minutes has been found to convert the calcium carbonate to calcium oxide by the very nature of the subsequent reactions when the sintered mass converts to a powdery mass on absorbing of atmospheric moisture. For larger pieces with larger cores than those defined and illustrated in the literature (cf. chapter 6), the soaking period may necessarily be of a longer duration, which can be determined by empirical testing

Feeder: a reservoir of molten metal to compensate for contraction of metal as it solidifies.

Firing: the heating of items to a high temperature in a kiln. In this investigation firing is understood to be firing test formula in an electric kiln to between 900^0C and 1000^0C.

Grog: an alumina-silicate that has been high fired to 1300^0C, which is used as an inert refractory particle in the ceramic shell investment process.

Hydrated lime: Calcium oxide that has been converted to calcium hydroxide by the action of water is called hydrated lime.

Hydrolysis: reactant + water $\longrightarrow$ (part of reactant + H) + (part of reactant + OH)

Investment: a semi-liquid, mixture consisting of a graded refractory filler, a binder and a liquid vehicle, which can be poured around the pattern and will conform exactly to the pattern shape and will subsequently set hard to form a mould.

Kieselguhr: a raw material found in nature in specific localities. It originates from the deposition of silica bearing diatoms.

Kulubrite-10: a branded grade of calcium carbonate (cf. product literature in the appendix V).

Levasil 4063: a colloidal silica sol product manufactured by Bayer AC Leverkusen, Germany (appendix VIII).

LG2 bronze alloy: an alloy comprising of 85% copper, 5% tin, 5% zinc and 5% lead.

LG4 bronze alloy: an alloy comprising of 87% copper, 7% tin, 3% zinc and 3% lead.

Lost wax: Cire perdue, the method of making a metal casting via a wax pattern.

Luto casting investment: a mixture of refractory materials mixed with plaster of paris which is used to make a refractory shell around a wax model.

Luto: The mixture of grog (chamotte) and plaster of paris used after it has been baked.

Mesh: the coarseness or fineness of particles, as measured by a metal screen through which they pass.

Microcrystalline wax: a synthetic wax being produced as a by-product in the petro-refining industry. The crystals in its structure are smaller than natural waxes or paraffin and this is described as microcrystalline wax. The melting point is 65^0C, but a much higher temperature is required to make the wax fluid so that it easily runs out of the heated mould.

Mortar : a mixture or cement with sand and water, used to bond bricks or stones into a structure.

Mould: The negative or female form from which a casting is made.

Orton cone: a branded pyrometric slumping cone that indicates the time-temperature relationship that has occurred in the item that has been heated to a certain temperature. Cone 010 is equivalent to 900^0C, 08 is equivalent to 945^0C and 06 is equivalent to 1000^0C.

Pins: zinc coated iron nails are placed through the wax model so that they penetrate the core and protrude out of the wax model so that the investment secures them to the core when the wax is burnt away during the de-wax process..

PPC: an abbreviation for Pretoria Portland Cement.

PET: Port Elizabeth Technikon, Republic of South Africa.

Porosity: In bronze casting; unsoundness of a casting due to the presence of blowholes, gas holes or shrinkage cavities.

Quenching: heating a casting to a specific temperature and quenching it in water to achieve rapid cooling.

Quick lime: calcium oxide.

Quick-setting formula: this is a formula where the dry ingredients are thoroughly mixed together and made into a pourable paste, using just enough de-ionized water to achieve this state. This fluid paste should set within six hours to enable the ceramic shell investment to commence.

Riser: A channel through which air escapes from the mould.

Runner: A channel through which metal enters the actual shape to be cast. In lost wax casting a wax rod is attached to the wax form before the mould is made.

Runner cup or sprue: The hollow at the top of a mould into which the metal is poured and from which the runners lead to the sculpture.

Sacrificial core: a core that when used in the lost wax process is removed to reveal a hollow cast.

Shellac: Varnish made from the resinous secretion of the Lac insect.

Sintering: this is taken to mean the coalescence under heat without liquefaction that is to bake and harden the ceramic shell without causing the shell to melt or fuse.

Sieve mesh sizes:

14 mesh = 1168 micron opening
100 mesh = 147 micron opening
200 mesh = 74 micron opening
325 mesh = 44 micron opening

Soaking (kiln): the kiln temperature is held at a specific temperature to achieve certain conditions in the item being heated.

Spalling: it is the disintegration that occurs in cement after the cement has been subjected to a fire (cf. detailed description in literature review 1.4.7).

Stucco: a process of sprinkling a wet, dip-coating of ceramic shell slurry with fine or medium grain sand.

Sintering temperature of the ceramic shell: the temperature required to sinter or convert the colloidal silica into a refractory structure is between 900^0C and 1000^0C (Young and Fennel,1986: 111).

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Levasil Product Literature: Levasil trial product AC 4063 Bayer, Leverkusen, Germany.

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Journals

The following journals have been perused for information pertaining to sacrificial and disintegrating cores in the ceramic shell process:

Castings S.A. 2000-2004 (inclusive). B. Crawford, (ed.), Johannesburg: BA Crawford Specialised Publications (Pty) Ltd. Published monthly. (48 journals)

Sculpture, 2000-2004 (inclusive). Editorial office: Washington, D.C. 20036, a publication of the International Sculpture Centre, published monthly by the International Sculpture Centre. (48 journals)

Interviews

Discussions have been held (*inter alia*) with the following persons:

Prof. N.P.L. Allen, Dean of the Faculty of Art and Design, PET.

Mr D.A. Jones, senior lecturer in the department of Studio Arts, Faculty of Art and Design, PET.

Mr H. Potgieter, senior chemist at PPC (Pretoria Portland Cement), Port Elizabeth.

Patents

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US Pat No 6428740 Dunyak, T.J. 2002 Method of Removing Cores from Ceramic Matrix Composite Articles. Washington: United States Patent Office.

US Pat No 4840219 Foreman, R.W. 1989 Mixture and Method for Preparing Casting Cores Prepared Thereby. Washington: United States Patent Office.

US Pat No 6221235 Gebhart, L.E. 2001 Removal of Sacrificial Cores by Electrochemical machining. Washington: United States Patent Office.

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US Pat. No 4108931 Ogden, R. 1978. System of Making Moulds for Investment Casting. Washington: United States Patent Office.

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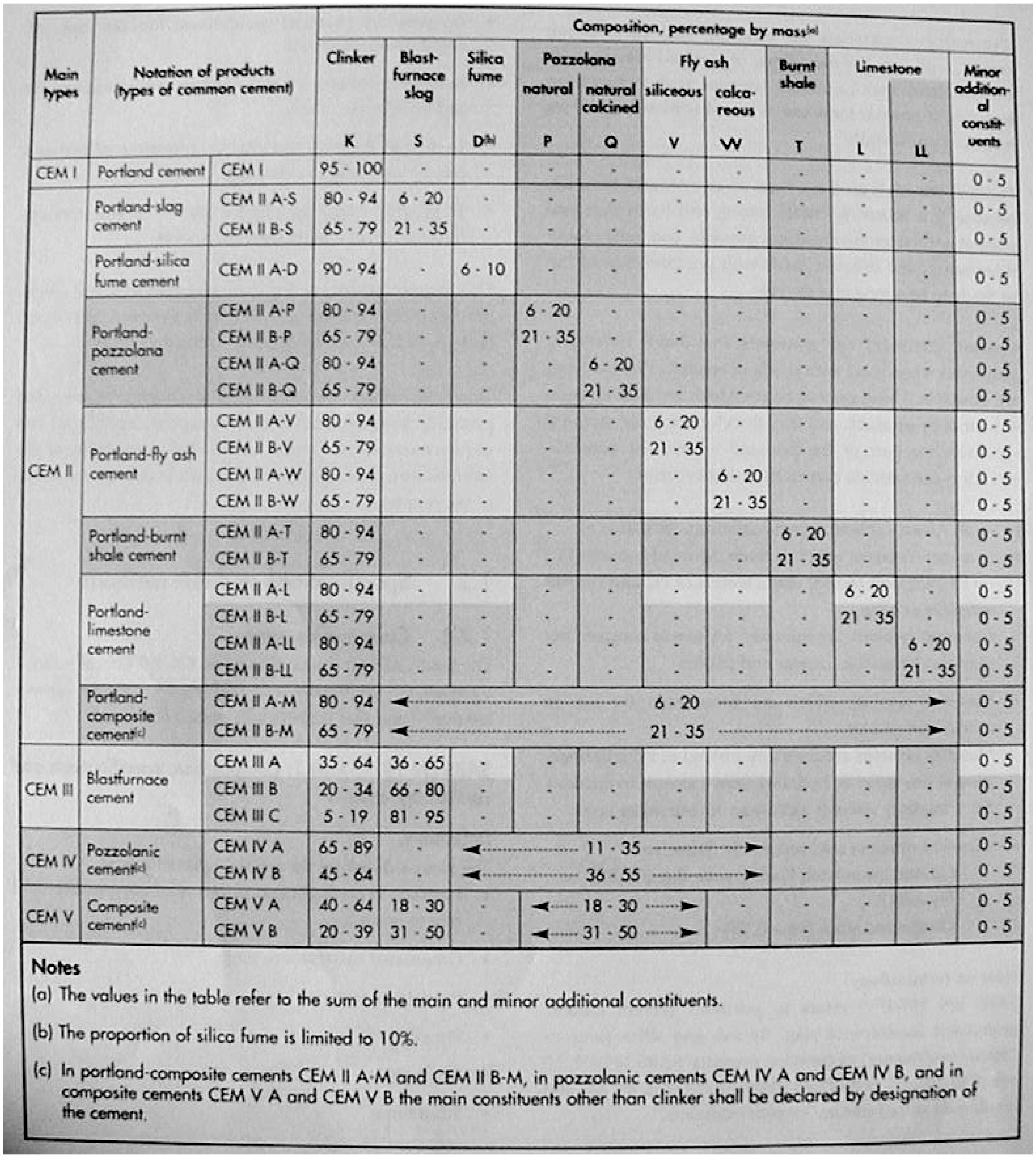
Appendices

Appendix I

Cem 11/ A-L 32.5 Portland limestone cement



Main types	Notation of products (types of common cement)		Composition, percentage by mass[a]										
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		Minor additional constituents
						natural	natural calcined	siliceous	calcareous				
			K	S	D[b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95 - 100	-	-	-	-	-	-	-	-	-	0 - 5
CEM II	Portland-slag cement	CEM II A-S	80 - 94	6 - 20	-	-	-	-	-	-	-	-	0 - 5
		CEM II B-S	65 - 79	21 - 35	-	-	-	-	-	-	-	-	0 - 5
	Portland-silica fume cement	CEM II A-D	90 - 94	-	6 - 10	-	-	-	-	-	-	-	0 - 5
	Portland-pozzolana cement	CEM II A-P	80 - 94	-	-	6 - 20	-	-	-	-	-	-	0 - 5
		CEM II B-P	65 - 79	-	-	21 - 35	-	-	-	-	-	-	0 - 5
		CEM II A-Q	80 - 94	-	-	-	6 - 20	-	-	-	-	-	0 - 5
		CEM II B-Q	65 - 79	-	-	-	21 - 35	-	-	-	-	-	0 - 5
	Portland-fly ash cement	CEM II A-V	80 - 94	-	-	-	-	6 - 20	-	-	-	-	0 - 5
		CEM II B-V	65 - 79	-	-	-	-	21 - 35	-	-	-	-	0 - 5
		CEM II A-W	80 - 94	-	-	-	-	-	6 - 20	-	-	-	0 - 5
		CEM II B-W	65 - 79	-	-	-	-	-	21 - 35	-	-	-	0 - 5
	Portland-burnt shale cement	CEM II A-T	80 - 94	-	-	-	-	-	-	6 - 20	-	-	0 - 5
		CEM II B-T	65 - 79	-	-	-	-	-	-	21 - 35	-	-	0 - 5
	Portland-limestone cement	CEM II A-L	80 - 94	-	-	-	-	-	-	-	6 - 20	-	0 - 5
		CEM II B-L	65 - 79	-	-	-	-	-	-	-	21 - 35	-	0 - 5
		CEM II A-LL	80 - 94	-	-	-	-	-	-	-	-	6 - 20	0 - 5
		CEM II B-LL	65 - 79	-	-	-	-	-	-	-	-	21 - 35	0 - 5
	Portland-composite cement[c]	CEM II A-M	80 - 94	◄ 6 - 20 ►									0 - 5
		CEM II B-M	65 - 79	◄ 21 - 35 ►									0 - 5
CEM III	Blastfurnace cement	CEM III A	35 - 64	36 - 65	-	-	-	-	-	-	-	-	0 - 5
		CEM III B	20 - 34	66 - 80	-	-	-	-	-	-	-	-	0 - 5
		CEM III C	5 - 19	81 - 95	-	-	-	-	-	-	-	-	0 - 5
CEM IV	Pozzolanic cement[c]	CEM IV A	65 - 89	-	◄ 11 - 35 ►					-	-	-	0 - 5
		CEM IV B	45 - 64	-	◄ 36 - 55 ►					-	-	-	0 - 5
CEM V	Composite cement[c]	CEM V A	40 - 64	18 - 30	-	◄ 18 - 30 ►			-	-	-	-	0 - 5
		CEM V B	20 - 39	31 - 50	-	◄ 31 - 50 ►			-	-	-	-	0 - 5

Notes

(a) The values in the table refer to the sum of the main and minor additional constituents.

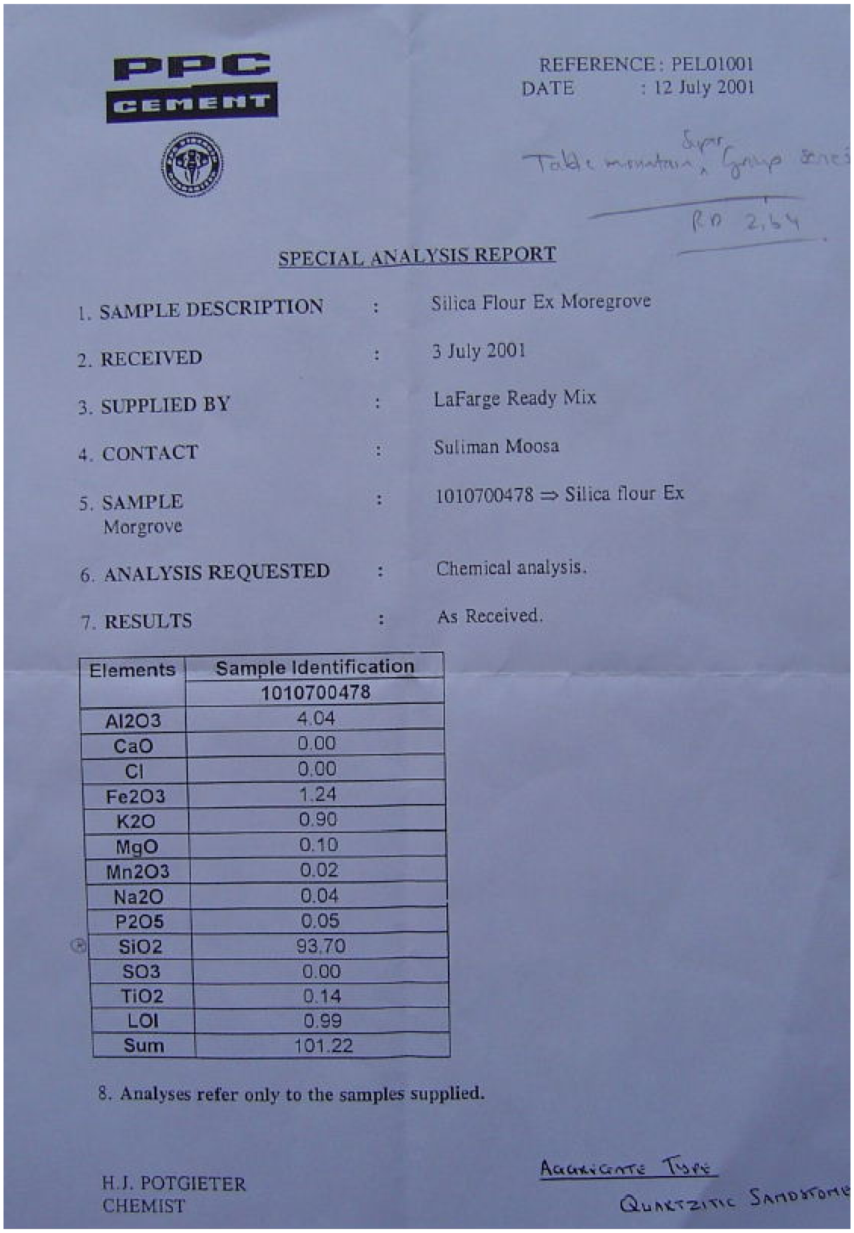
(b) The proportion of silica fume is limited to 10%.

(c) In portland-composite cements CEM II A-M and CEM II B-M, in pozzolanic cements CEM IV A and CEM IV B, and in composite cements CEM V A and CEM V B the main constituents other than clinker shall be declared by designation of the cement.

A single 50 kg bag of branded Surebuild cement was used throughout this investigation. Surebuild cement complies with the SABS ENV 197, CEM 11/ A – L 32,5 and is defined as having 6-20% limestone, 80-94% clinker and 0-5% minor additional constituents.

Appendix II

Silica 0,074 mm



PPC CEMENT

REFERENCE : PEL01001
DATE : 12 July 2001

Table mountain Super Group series

RD 2,64

SPECIAL ANALYSIS REPORT

1. SAMPLE DESCRIPTION : Silica Flour Ex Moregrove
2. RECEIVED : 3 July 2001
3. SUPPLIED BY : LaFarge Ready Mix
4. CONTACT : Suliman Moosa
5. SAMPLE Morgrove : 1010700478 ⇒ Silica flour Ex
6. ANALYSIS REQUESTED : Chemical analysis.
7. RESULTS : As Received.

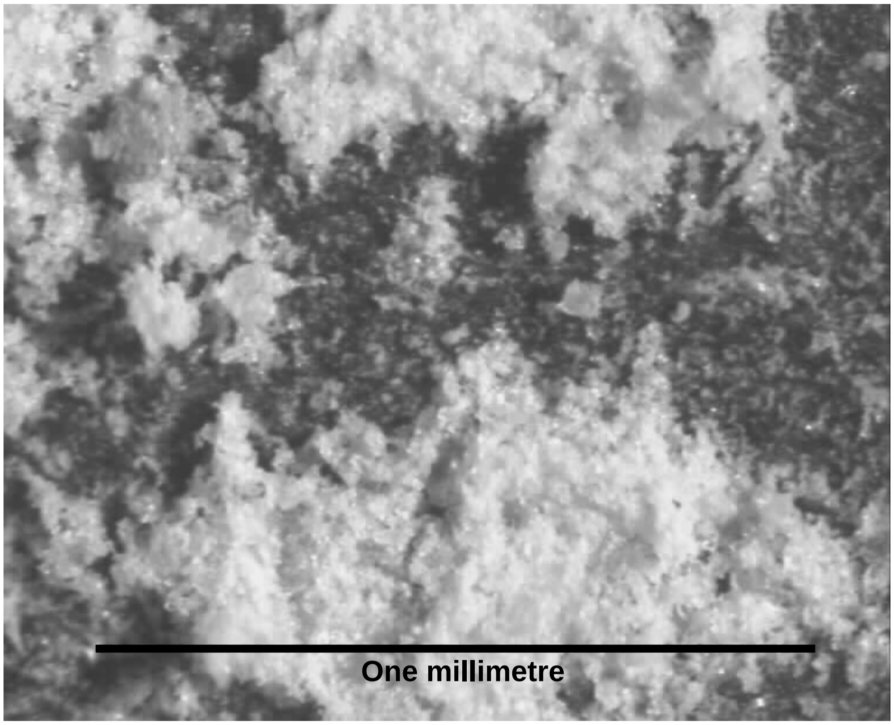
Elements	Sample Identification
	1010700478
Al2O3	4.04
CaO	0.00
Cl	0.00
Fe2O3	1.24
K2O	0.90
MgO	0.10
Mn2O3	0.02
Na2O	0.04
P2O5	0.05
SiO2	93.70
SO3	0.00
TiO2	0.14
LOI	0.99
Sum	101.22

8. Analyses refer only to the samples supplied.

H.J. POTGIETER
CHEMIST

AGGREGATE TYPE
QUARTZITIC SANDSTONE

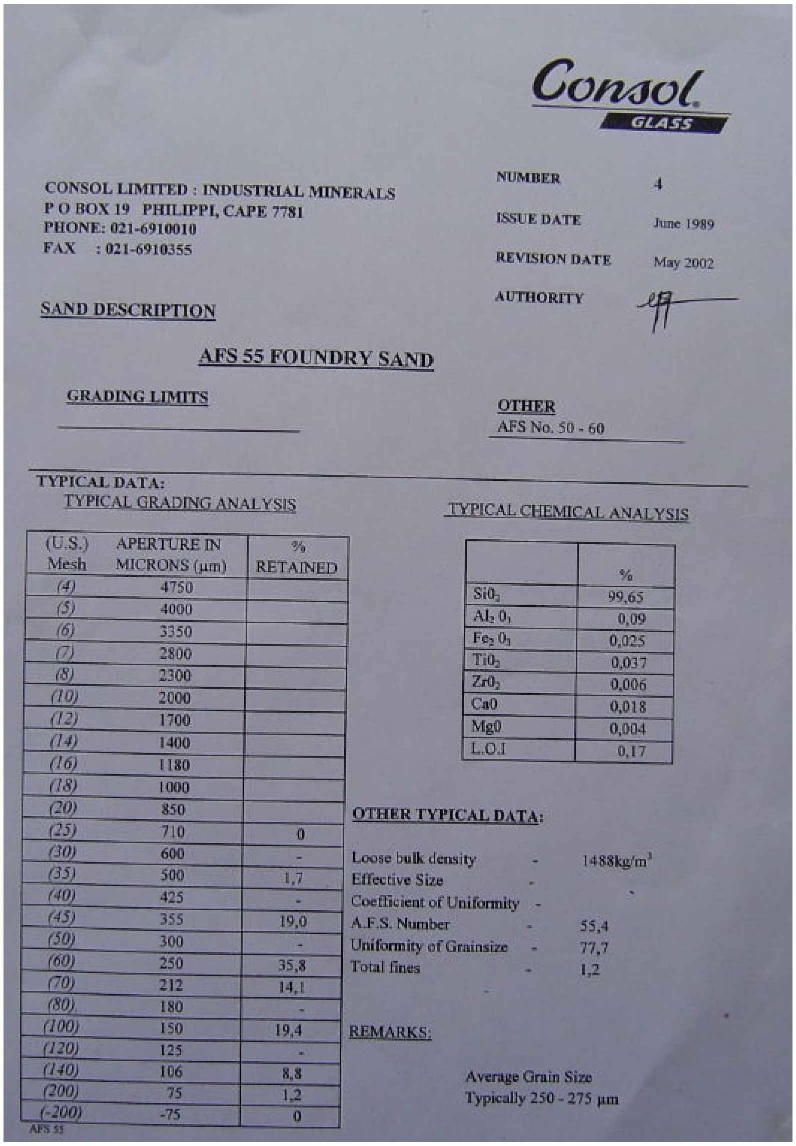
A single 50 kg bag of silica flour 0,074 mm was used throughout this investigation. The silica flour was sourced fro LaFarge Ready Mix, ex Moregrove, Port Elizabeth.



A photograph of silica 0,074 mm (silica flour) as supplied by LaFarge Ready Mix, Moregrove, Port Elizabeth, with an analysis of 93.7% SiO_2 and 4,04% Al_2O_3.

Appendix III

Silica 0,2 mm



Consol GLASS

CONSOL LIMITED : INDUSTRIAL MINERALS
P O BOX 19 PHILIPPI, CAPE 7781
PHONE: 021-6910010
FAX : 021-6910355

NUMBER 4

ISSUE DATE June 1989

REVISION DATE May 2002

AUTHORITY

SAND DESCRIPTION

AFS 55 FOUNDRY SAND

GRADING LIMITS

OTHER
AFS No. 50 - 60

TYPICAL DATA:

TYPICAL GRADING ANALYSIS

(U.S.) Mesh	APERTURE IN MICRONS (µm)	% RETAINED
(4)	4750	
(5)	4000	
(6)	3350	
(7)	2800	
(8)	2300	
(10)	2000	
(12)	1700	
(14)	1400	
(16)	1180	
(18)	1000	
(20)	850	
(25)	710	0
(30)	600	-
(35)	500	1,7
(40)	425	-
(45)	355	19,0
(50)	300	-
(60)	250	35,8
(70)	212	14,1
(80)	180	-
(100)	150	19,4
(120)	125	-
(140)	106	8,8
(200)	75	1,2
(-200)	-75	0

AFS 55

TYPICAL CHEMICAL ANALYSIS

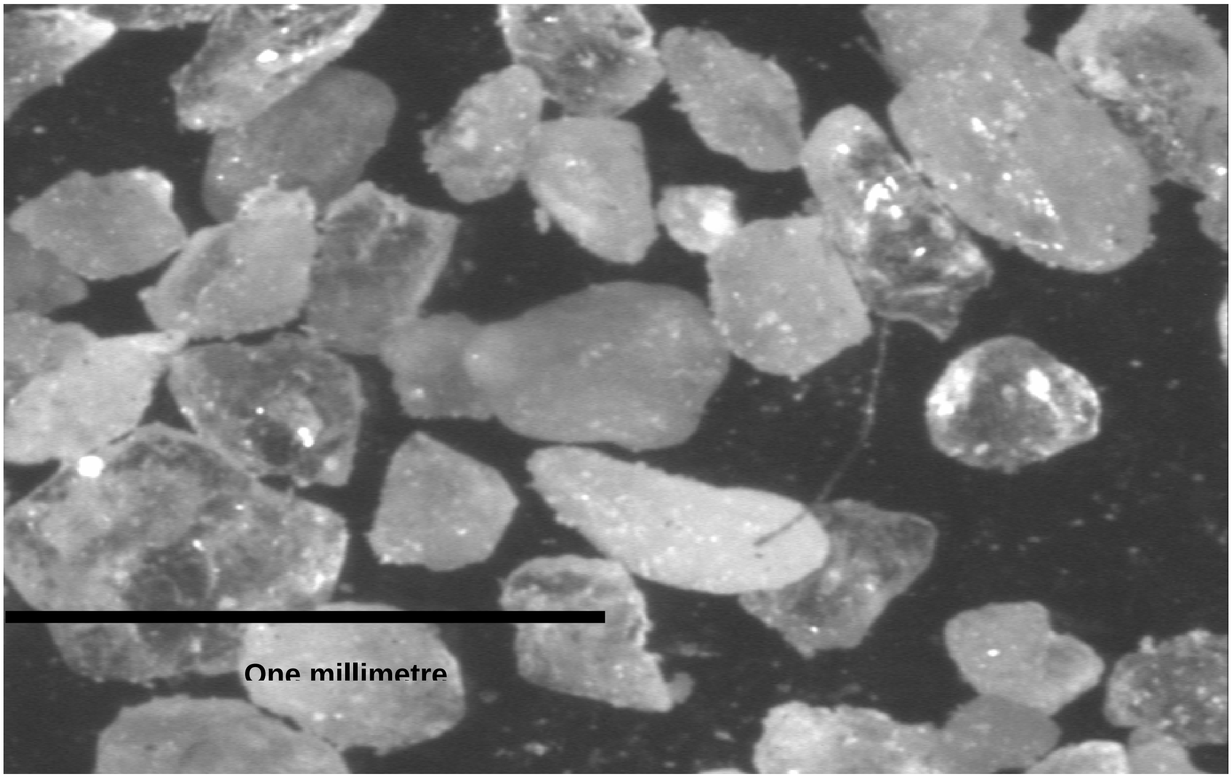
	%
$Si0_2$	99,65
$Al_2 0_3$	0,09
$Fe_2 0_3$	0,025
$Ti0_2$	0,037
$Zr0_2$	0,006
Ca0	0,018
Mg0	0,004
L.O.I	0,17

OTHER TYPICAL DATA:

Loose bulk density	-	1488kg/m^3
Effective Size	-	
Coefficient of Uniformity	-	
A.F.S. Number	-	55,4
Uniformity of Grainsize	-	77,7
Total fines	-	1,2

REMARKS:

Average Grain Size
Typically 250 - 275 µm

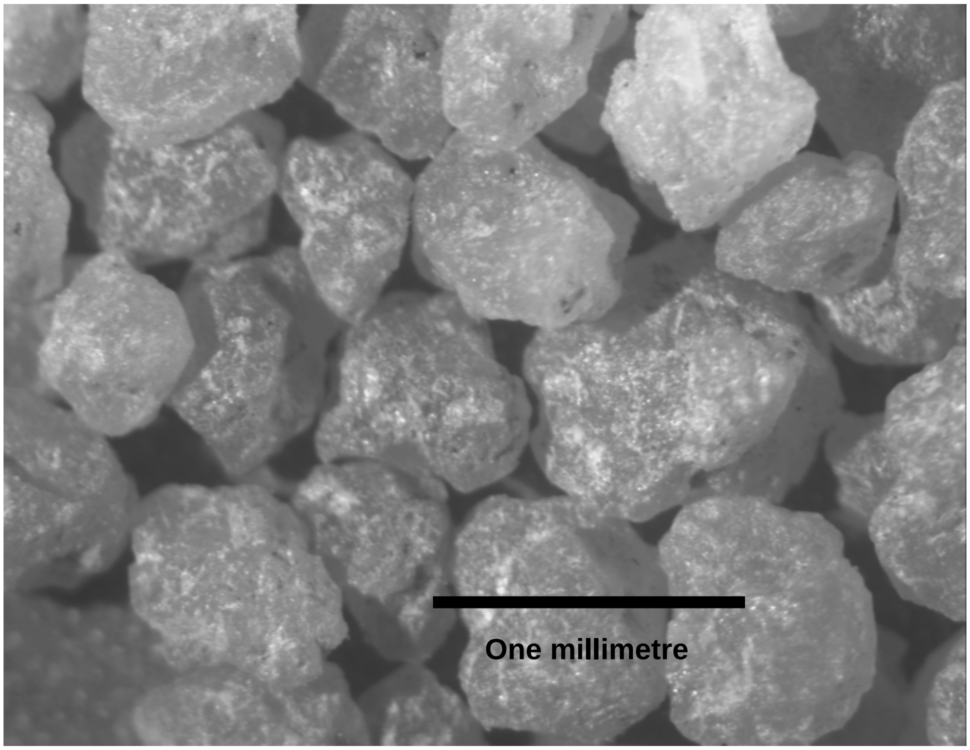


A single 40 kg bag of ASF 55 foundry sand was used throughout this investigation.

A photograph of the graded silica 0,2 mm that was used in this investigation. It has a specification of 99,65% SiO_2 and 0,09% Al_2O_3 with a typical grain size 250-275 microns, supplied by Consol Limited, PO Box 19, Phillipi, Cape Town 7781.

Appendix IV

Silica 0,95 mm

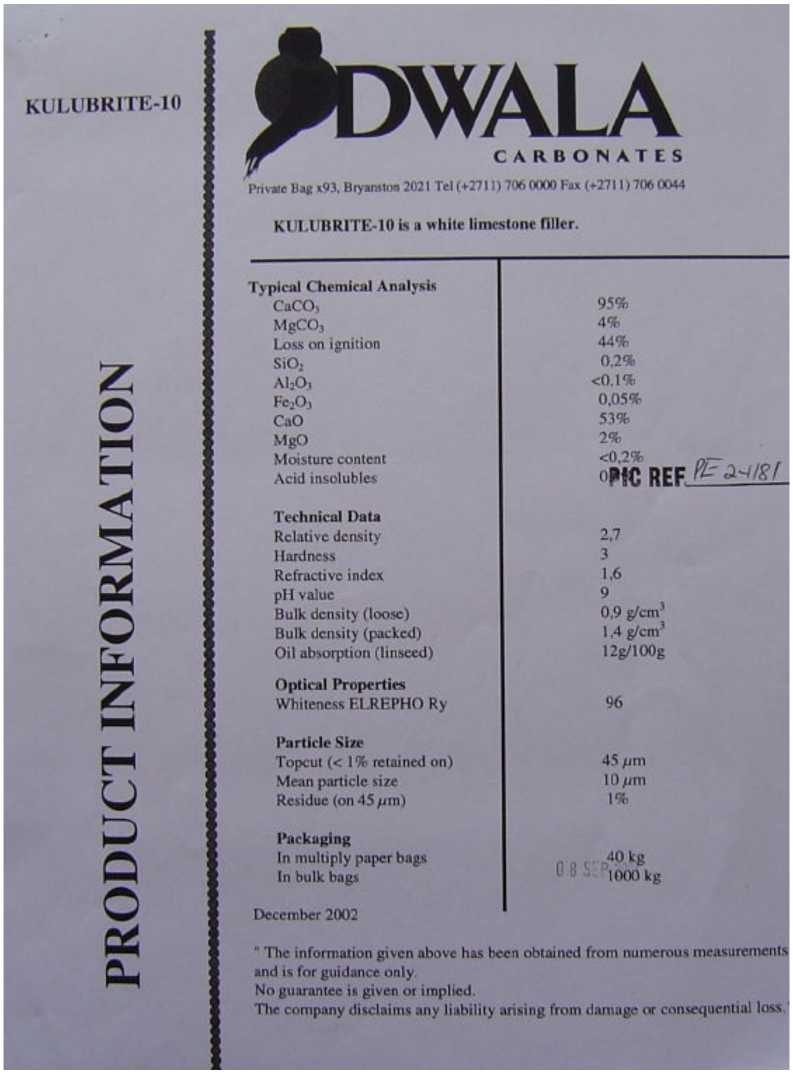


A single 50 kg bag of branded B @ E silica was used throughout this investigation.

A photograph of graded silica 0,95 mm that was used throughout this investigation with a specification of 0,95 mm silica sand with a uniformity coefficient of < 1.40. Packed by B and E Silica (Pty) Ltd, Delmas, 2210 and graded at SiO_2 + 98%.

Appendix V

Calcium carbonate



PRODUCT INFORMATION

KULUBRITE-10

DWALA

CARBONATES

Private Bag x93, Bryanston 2021 Tel (+2711) 706 0000 Fax (+2711) 706 0044

KULUBRITE-10 is a white limestone filler.

Typical Chemical Analysis	
$CaCO_3$	95%
$MgCO_3$	4%
Loss on ignition	44%
SiO_2	0,2%
Al_2O_3	<0,1%
Fe_2O_3	0,05%
CaO	53%
MgO	2%
Moisture content	<0,2%
Acid insolubles	0
Technical Data	
Relative density	2,7
Hardness	3
Refractive index	1,6
pH value	9
Bulk density (loose)	0,9 g/cm^3
Bulk density (packed)	1,4 g/cm^3
Oil absorption (linseed)	12g/100g
Optical Properties	
Whiteness ELREPHO Ry	96
Particle Size	
Topcut (< 1% retained on)	45 μm
Mean particle size	10 μm
Residue (on 45 μm)	1%
Packaging	
In multiply paper bags	40 kg
In bulk bags	1000 kg

PIC REF PE 24181

08 SEP

December 2002

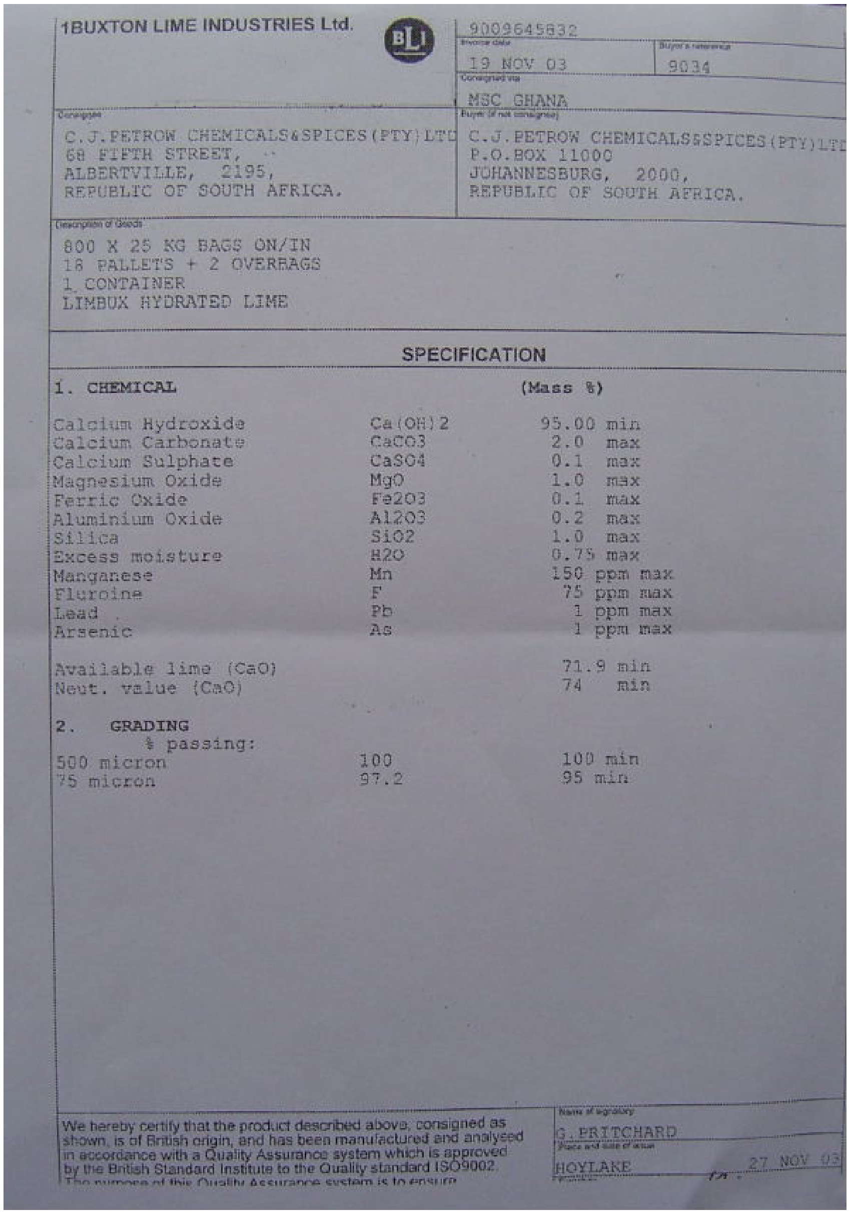
" The information given above has been obtained from numerous measurements and is for guidance only.
No guarantee is given or implied.
The company disclaims any liability arising from damage or consequential loss.

A single bag of Kulubrite-10 was used throughout this investigation.

The calcium carbonate is sold under the trade name as Kulubrite-10 and contains 95% calcium carbonate and 4% magnesium carbonate with a loss on ignition of 44%.

Appendix VI

Calcium hydroxide



1BUXTON LIME INDUSTRIES Ltd.

9009645832

Invoice date: 19 NOV 03
Buyer's reference: 9034
Consigned via: MSC GHANA

Consignee:
C.J.PETROW CHEMICALS&SPICES(PTY)LTD
68 FIFTH STREET,
ALBERTVILLE, 2195,
REPUBLIC OF SOUTH AFRICA.

Buyer (if not consignee):
C.J.PETROW CHEMICALS&SPICES(PTY)LT
P.O.BOX 11000
JOHANNESBURG, 2000,
REPUBLIC OF SOUTH AFRICA.

Description of Goods:
800 X 25 KG BAGS ON/IN
18 PALLETS + 2 OVERBAGS
1 CONTAINER
LIMBUX HYDRATED LIME

SPECIFICATION

1. CHEMICAL		**(Mass %)**
Calcium Hydroxide	Ca(OH)2	95.00 min
Calcium Carbonate	CaCO3	2.0 max
Calcium Sulphate	CaSO4	0.1 max
Magnesium Oxide	MgO	1.0 max
Ferric Oxide	Fe2O3	0.1 max
Aluminium Oxide	Al2O3	0.2 max
Silica	SiO2	1.0 max
Excess moisture	H2O	0.75 max
Manganese	Mn	150 ppm max
Fluroine	F	75 ppm max
Lead	Pb	1 ppm max
Arsenic	As	1 ppm max
Available lime (CaO)		71.9 min
Neut. value (CaO)		74 min
2. GRADING		
% passing:		
500 micron	100	100 min
75 micron	97.2	95 min

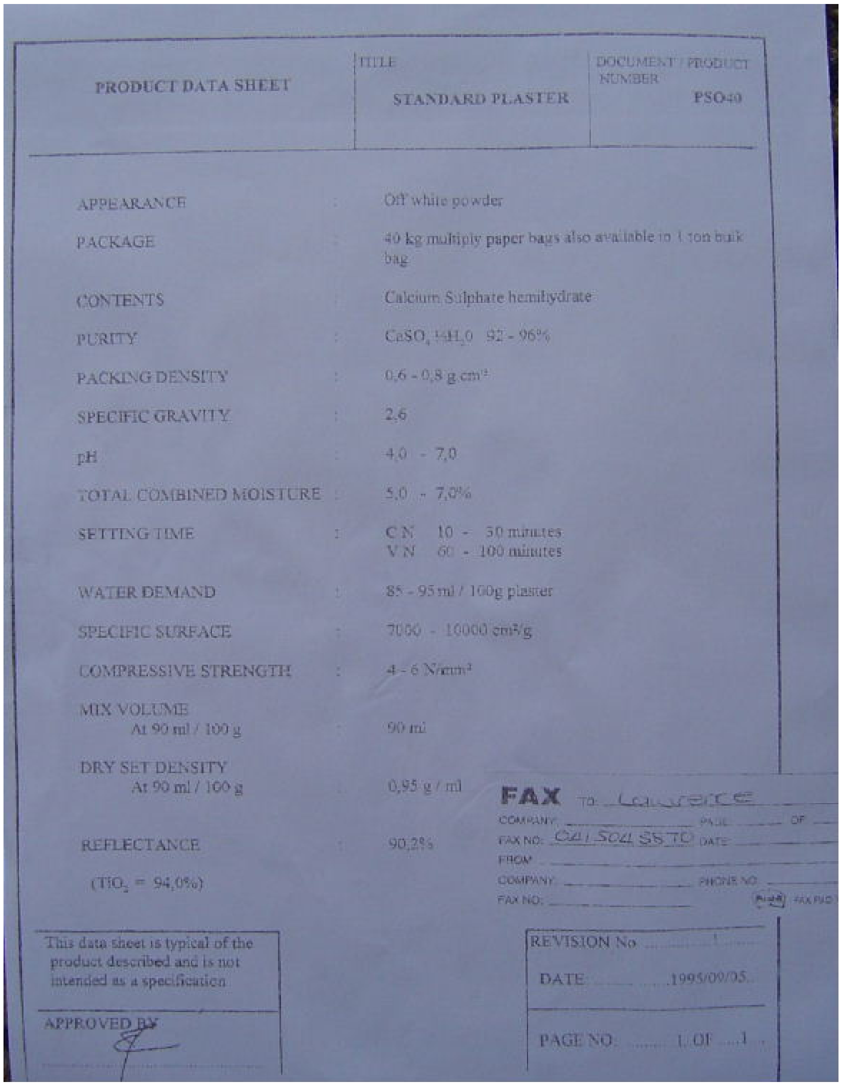
We hereby certify that the product described above, consigned as shown, is of British origin, and has been manufactured and analysed in accordance with a Quality Assurance system which is approved by the British Standard Institute to the Quality standard ISO9002. The purpose of this Quality Assurance system is to ensure

Name of signatory: G. PRITCHARD
Place and date of issue: HOYLAKE 27 NOV 03

A single 50 kg bag of branded Limbux Hydrated Lime was used in this investigation. It has a 95.0% minimum content of calcium hydroxide and a maximum of 2,0% calcium carbonate.

Appendix VII

Plaster of paris



PRODUCT DATA SHEET	TITLE STANDARD PLASTER	DOCUMENT / PRODUCT NUMBER PSO40

APPEARANCE	:	Off white powder
PACKAGE	:	40 kg multiply paper bags also available in 1 ton bulk bag
CONTENTS	:	Calcium Sulphate hemihydrate
PURITY	:	$CaSO_4 \frac{1}{2}H_2O$ 92 - 96%
PACKING DENSITY	:	0,6 - 0,8 g.cm^{-3}
SPECIFIC GRAVITY	:	2,6
pH	:	4,0 - 7,0
TOTAL COMBINED MOISTURE	:	5,0 - 7,0%
SETTING TIME	:	C N 10 - 30 minutes V N 60 - 100 minutes
WATER DEMAND	:	85 - 95 ml / 100g plaster
SPECIFIC SURFACE	:	7000 - 10000 cm²/g
COMPRESSIVE STRENGTH	:	4 - 6 N/mm²
MIX VOLUME At 90 ml / 100 g	:	90 ml
DRY SET DENSITY At 90 ml / 100 g	:	0,95 g / ml
REFLECTANCE (TiO_2 = 94,0%)	:	90,2%

FAX TO: Lawrence
COMPANY: PAGE OF
FAX NO: 041 504 5570 DATE:
FROM:
COMPANY: PHONE NO:
FAX NO:

This data sheet is typical of the product described and is not intended as a specification

APPROVED BY

REVISION No ....1.....

DATE ....1995/09/05..

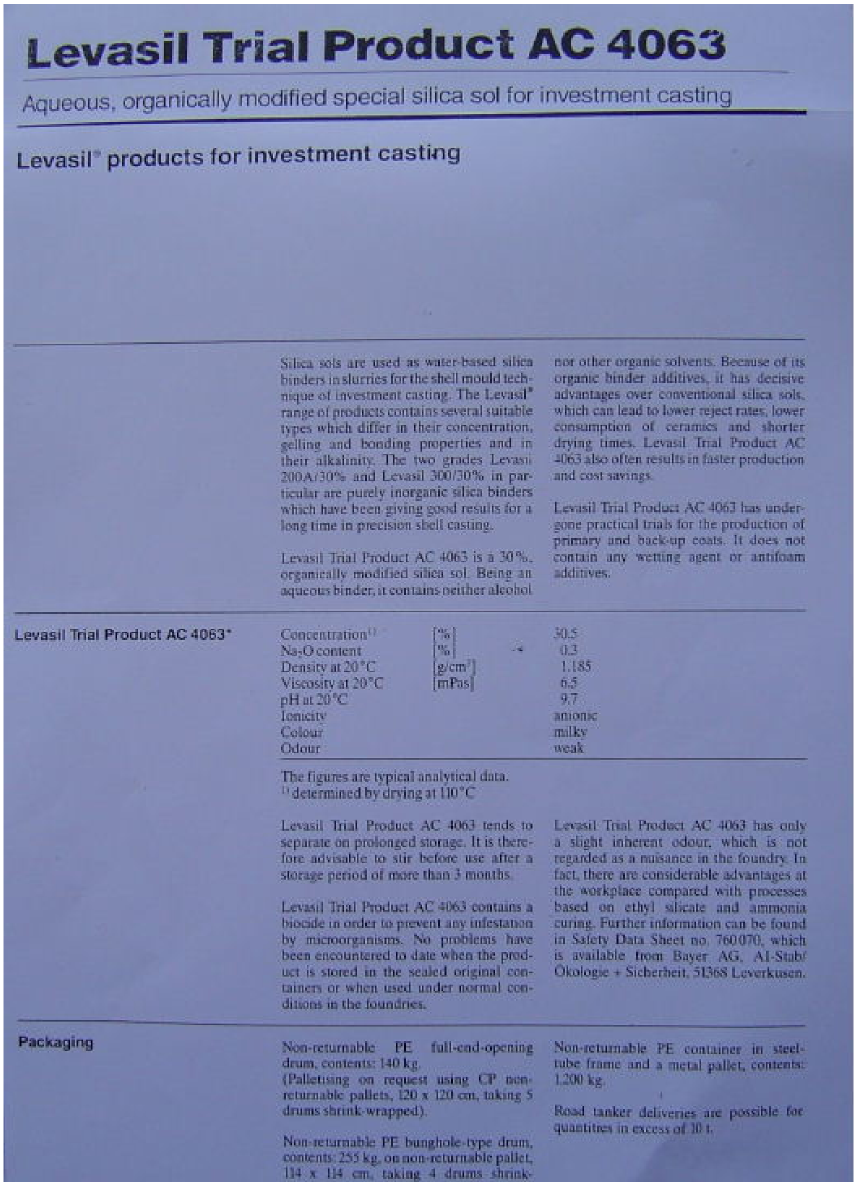
PAGE NO. .... 1 OF 1

A single 40 kg bag of branded BPB standard plaster was used throughout this investigation.

Plaster of paris, BPB plaster is manufactured by BPB Rhinoboard division obtainable from Cape Town or local gypsum suppliers. The calcium sulphate hemi-hydrate has a purity of between 92 – 96%.

Appendix VIII

Levasil 4063



Levasil Trial Product AC 4063

Aqueous, organically modified special silica sol for investment casting

Levasil® products for investment casting

Silica sols are used as water-based silica binders in slurries for the shell mould technique of investment casting. The Levasil® range of products contains several suitable types which differ in their concentration, gelling and bonding properties and in their alkalinity. The two grades Levasil 200A/30% and Levasil 300/30% in particular are purely inorganic silica binders which have been giving good results for a long time in precision shell casting.

Levasil Trial Product AC 4063 is a 30%, organically modified silica sol. Being an aqueous binder, it contains neither alcohol nor other organic solvents. Because of its organic binder additives, it has decisive advantages over conventional silica sols, which can lead to lower reject rates, lower consumption of ceramics and shorter drying times. Levasil Trial Product AC 4063 also often results in faster production and cost savings.

Levasil Trial Product AC 4063 has undergone practical trials for the production of primary and back-up coats. It does not contain any wetting agent or antifoam additives.

Levasil Trial Product AC 4063*

Concentration[1]	[%]	30.5
Na_2O content	[%]	0.3
Density at 20°C	[g/cm³]	1.185
Viscosity at 20°C	[mPas]	6.5
pH at 20°C		9.7
Ionicity		anionic
Colour		milky
Odour		weak

The figures are typical analytical data.
[1] determined by drying at 110°C

Levasil Trial Product AC 4063 tends to separate on prolonged storage. It is therefore advisable to stir before use after a storage period of more than 3 months.

Levasil Trial Product AC 4063 contains a biocide in order to prevent any infestation by microorganisms. No problems have been encountered to date when the product is stored in the sealed original containers or when used under normal conditions in the foundries.

Levasil Trial Product AC 4063 has only a slight inherent odour, which is not regarded as a nuisance in the foundry. In fact, there are considerable advantages at the workplace compared with processes based on ethyl silicate and ammonia curing. Further information can be found in Safety Data Sheet no. 760070, which is available from Bayer AG, AI-Stab/Ökologie + Sicherheit, 51368 Leverkusen.

Packaging

Non-returnable PE full-end-opening drum, contents: 140 kg.
(Palletising on request using CP non-returnable pallets, 120 x 120 cm, taking 5 drums shrink-wrapped).

Non-returnable PE bunghole-type drum, contents: 255 kg, on non-returnable pallet, 114 x 114 cm, taking 4 drums shrink-

Non-returnable PE container in steel-tube frame and a metal pallet, contents: 1,200 kg.

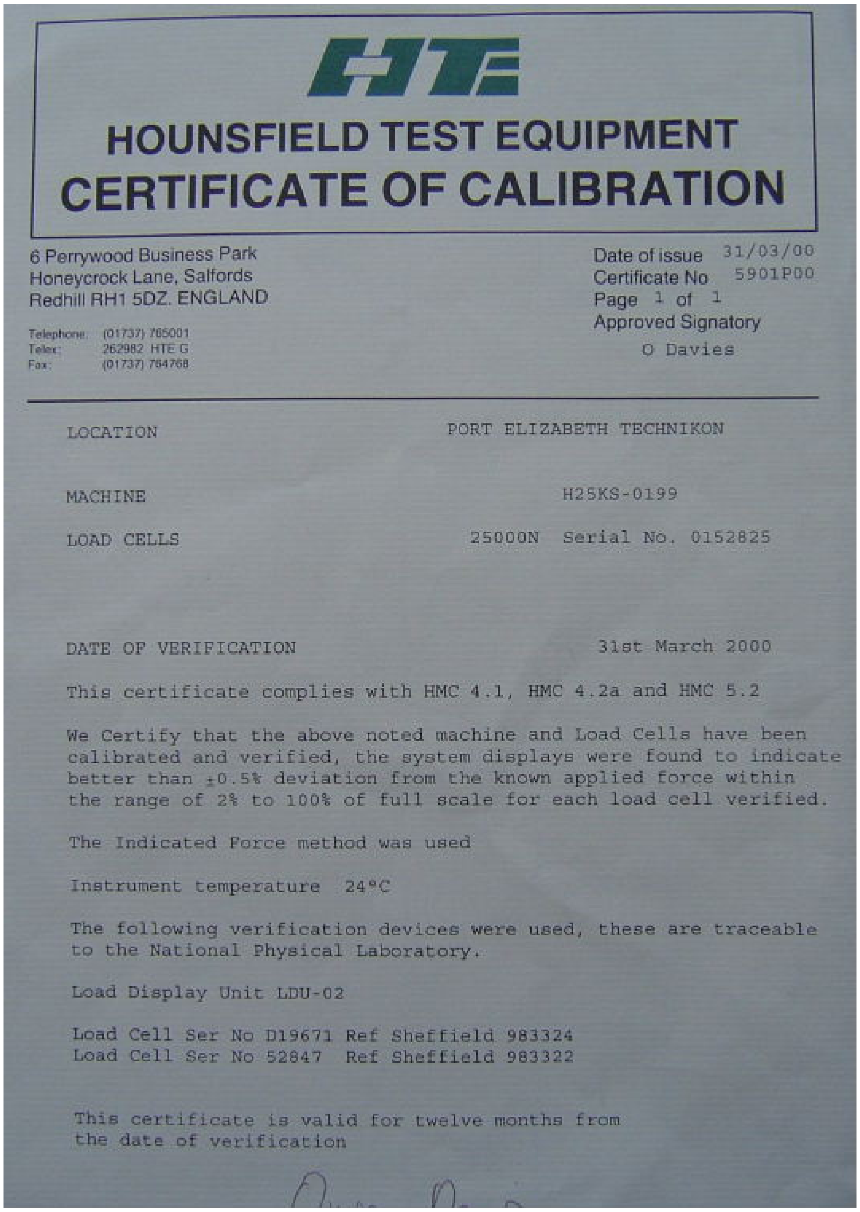
Road tanker deliveries are possible for quantities in excess of 10 t.

Levasil 4063 was used throughout this investigation as an investment ingredient.

It is mixed with 60% by chamotte 200 mesh powder to form a slurry, which with a stucco of chamotte 0,2 to 0,7 mm is applied as an investment to the wax model in the bronze casting process.

Appendix IX

Hounsfield test equipment



HOUNSFIELD TEST EQUIPMENT

CERTIFICATE OF CALIBRATION

6 Perrywood Business Park
Honeycrock Lane, Salfords
Redhill RH1 5DZ. ENGLAND

Telephone: (01737) 765001
Telex: 262982 HTE G
Fax: (01737) 764768

Date of issue 31/03/00
Certificate No 5901P00
Page 1 of 1
Approved Signatory
O Davies

LOCATION PORT ELIZABETH TECHNIKON

MACHINE H25KS-0199

LOAD CELLS 25000N Serial No. 0152825

DATE OF VERIFICATION 31st March 2000

This certificate complies with HMC 4.1, HMC 4.2a and HMC 5.2

We Certify that the above noted machine and Load Cells have been calibrated and verified, the system displays were found to indicate better than ±0.5% deviation from the known applied force within the range of 2% to 100% of full scale for each load cell verified.

The Indicated Force method was used

Instrument temperature 24°C

The following verification devices were used, these are traceable to the National Physical Laboratory.

Load Display Unit LDU-02

Load Cell Ser No D19671 Ref Sheffield 983324
Load Cell Ser No 52847 Ref Sheffield 983322

This certificate is valid for twelve months from the date of verification

A certificate of calibration illustrating this equipment is regularly maintained. It was used to measure compression values in chapter 6.

The computer programme to operate the Hounsfield apparatus is as follows:

↓

Password- enter
Test-zone-click X2
File-
Open test method-clickx2
Compression-OK

Brick
Date operator batch
Settings
Load range 250
Displacement range 10
Speed 20
On-OK

Test spec 1
Diameter 10-OK
Test specimen, 1-click repeat for all the tests
File
Exit sure-yes
Save results-OK

To enter information above go to:
QMAT file exam
Open test
Compression
Brick
View results type batch 4SX

test
display
select all
feathery icon
file
export curves
destination excel OK
file programs
Excel
file
PUT IN DISC
Save in 3,5
Call 4SX
Save