

**The Feasibility of
Reclaiming Shell Material
From Investment
Castings**

**Timothy M. Peters
Daniel L. Twarog
University of Illinois**

About WMRC's Electronic Publications:

This document was originally published in a traditional format.

It has been transferred to an electronic format to allow faster and broader access to important information and data.

While the Center makes every effort to maintain a level of quality during the transfer from print to digital format, it is possible that minor formatting and typographical inconsistencies will still exist in this document.

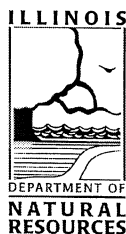
Additionally, due to the constraints of the electronic format chosen, page numbering will vary slightly from the original document.

The original, printed version of this document may still be available.

Please contact WMRC for more information:

**WMRC
One E. Hazelwood Drive
Champaign, IL 61820
217-333-8940 (phone)**

www.wmrc.uiuc.edu



WMRC is a division of the
Illinois Department of Natural
Resources

**The Feasibility of Reclaiming Investment Shell Material
from
Investment Castings**

by

Timothy M. Peters
University of Missouri-Rolla
Rolla, Missouri

and

Daniel L. Twarog
Director of Research
American Foundrymen's Society

Prepared for the

Hazardous Waste Research and Information Center
One East Hazelwood Drive
Champaign, Illinois 61820

HWRIC Project RRT-10

Printed by Authority of the State of Illinois

92/200

The mention of any trade name, commercial product, person, or activity does not constitute nor should it imply, an endorsement by HWRIC. Similarly, the exclusion of any trade name, commercial product, person, or activity does not constitute, nor should it imply, disapproval by HWRIC.

ACKNOWLEDGEMENTS

Grateful thanks is extended to the Illinois Hazardous Waste Research and Information Center and the American Foundrymens Society for the financial support making this work possible.

Thanks is also due to Dr. John Watson of the Metallurgical Engineering Department at the University of Missouri-Rolla and to Mr. Marvin Adams at the United States Bureau of Mines office at Rolla for the use of equipment and facilities.

The author gives sincere thanks to his advisor, Dr. Robert Moore, for direction, support and encouragement. Ms. Xiaoling Wang must be credited for her assistance with this manuscript and kind patience during this work.

Information contained in the mineral processing sections of this report are as taught by B.A. Wells in his excellent work, Mineral Processing Technology. Workers considering reclamation operations would be well advised to obtain this volume.

CONTENTS

ACKNOWLEDGEMENT	iii
TABLES	v
FIGURES	v
ABSTRACT	vi
EXECUTIVE SUMMARY	vii
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 INVESTMENT SHELL PROCESS DESCRIPTION	3
CHAPTER 3 INVESTMENT SHELL MATERIALS	5
CHAPTER 4 MATERIALS FACTORS OF INVESTMENT CASTING SHELLS	13
CHAPTER 5 INVESTMENT MATERIALS INDUSTRY SURVEY	17
CHAPTER 6 SHELL PHASE COMPOSITIONS	21
CHAPTER 7 LITERATURE SURVEY	25
CHAPTER 8 MINERAL PROCESSING FOR RECLAMATION	29
CHAPTER 9 CRUSHING TRIALS	33
CHAPTER 10 CLASSIFICATION	37
CHAPTER 11 CONCENTRATION PROCESSES	41
CHAPTER 12 HEAVY MEDIUM SEPARATORS	43
CHAPTER 13 RECLAMATION FACILITATING MODIFICATIONS	45
CHAPTER 14 CONCLUSIONS AND RECOMMENDATIONS	46
REFERENCES CITED	48
APPENDIX I SEM PHOTOGRAPHS OF STUCCO COMPOSITIONS	51
APPENDIX II OPTICAL MICROGRAPHS OF INVESTMENT SHELLS	56
APPENDIX III REFLECTED LIGHT MICROGRAPHS OF SPENT SHELLS	59
APPENDIX IV CATHODOLUMINESCENCE MICROGRAPHS OF SPENT SHELLS	62
GLOSSARY	67

TABLES

TABLE 1	FUSED SILICA-TYPICAL PARTICLE SIZE RANGES	6
TABLE 2	ALUMINOSILICATE STUCCO PRODUCTS	10
TABLE 3	PRIME COAT COMPOSITIONS	18
TABLE 4	BACKUP COAT COMPOSITIONS	18a

FIGURES

FIG. 1	THE INVESTMENT CASTING PROCESS	3
FIG. 2	INVESTMENT CASTING SHELL IN CROSS SECTION	5
FIG. 3	ZIRCON TIME-PRICE RELATIONSHIP	9
FIG. 4	U.S. ZIRCON CONSUMPTION, BY INDUSTRY	9
FIG. 5	EFFECT ON STABILITY OF pH AND IONIC CONTENT IN THE COLLOIDAL SILICA-WATER SYSTEM	11
FIG. 6	PHASE DISTRIBUTION GRAPH	23
FIG. 7	OVERALL PHASE COMPOSITION	24
FIG. 8	ORE FRAGMENT AND PRODUCTS OF COMMINUTION	29
FIG. 9	ROLL GEOMETRY	31
FIG. 10	SIEVE SCREEN PARTICLE SIZE ANALYSIS, FOUR ROLL SETTINGS	34
FIG. 11	XRD DIFFRACTION PATTERNS FOR 1/2 AND 1/8 ROLL GAPS	35
FIG. 12	APPARENT VISCOSITY-DENSITY RELATIONSHIP FOR HEAVY MEDIA SUSPENSIONS	44
FIG. 13	ONE AND TWO COMPARTMENT HEAVY MEDIUM CONTINUOUS PROCESS DRUM SEPARATORS	44

ABSTRACT

This report examines the feasibility of investment shell component reclamation. Shell material components and their compositions are investigated with an industry survey, a study of the available literature, and analysis of specimen shell materials. Physical properties and factors related to the reclamation and reuse of shell materials are described.

Well known mineral processing methods are capable of producing concentrates of the various shell components. The theory and techniques of some applicable processes are discussed to assist with the development of reclamation operations. The recommended methods are; comminution by roll crushing, component concentration by screening, gravity settling or heavy medium separation.

Aluminosilicate stucco (a major component of many investment shells) can be recovered in a form suitable for reuse as backup stucco. Zircon (a minor component in many shell compositions) can be concentrated in an impure form, and subsequent caustic liberation treatments can remove the intermixed silica phases. Reuse of such zircon in investment casting may be possible but will require careful qualification testing. Fused and crystalline silica (major components of most shell compositions) are not reusable for investment casting. The feasibility of reclamation will be influenced by individual foundry choices of materials, composition and shell practice.

EXECUTIVE SUMMARY

Purpose and Methods-

This report examines the feasibility of recovering investment shell components. Data on typical investment shell compositions, obtained from an industry survey, specimen, scanning electron microscope (SEM) and radiographic diffractive (XRD) analysis is presented. Material reclamation are discussed. Prior investigation and ongoing reclamation operations are reviewed. Mineral processing theory and methods are discussed to assist in the development of reclamation operations.

Investment Shell Materials-

The ceramic components of investment casting shells are typically used for one cycle of shell production and then are discarded. Most investment shell compositions comprise several or all of the following materials; fused silica, aluminosilicates of several compositions, and zircon. Shell wastes include cristobalite to this mixture. The value and reuse potential of each material is different.

Potential for Aluminosilicate Stucco Reclamation-

Aluminosilicate materials are widely employed in investment compositions, primarily as backup coat stucco, and constitute one half or more of the shell weight for form suited for reuse as backup stucco. Aluminosilicate stuccoes are tough composites of mullite ($3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) and glass, which are not usually degraded or damaged by investment casting processes. Stucco application methods should tolerate the introduction of a reclaimed product. Stucco may retain a partial coating of silica from the backup refractory. Shell component and processing variables can affect the feasibility of reclamation and reuse.

Potential for Zircon Reclamation-

Zircon, as fine powder and sand, is a minor component in many investment shell compositions; commonly used only in the critical but thin prime coats and often mixed with fine fused silica powders. It would be possible to concentrate zircon-rich shell fragments after crushing to a suitable size and subsequent caustic leaching can liberate a fairly pure zircon; however the particle size and the quantities present are disadvantages to processing. The investment casting

industry may have difficulty reusing leach-liberated zircon powders, due to contamination sensitivity of the colloidal silica slurry process.

Alternative applications for recovered zircon need to overcome many objections; including composition, form and quantities recovered. Most industries that use zircon depend on its excellent properties, controlled in part by the purity and particle size of available products. Users of lower grade zircons, perhaps prone to acceptance of a recycled material, have in general already been excluded from the market and have developed substitutes. The investment casting industry accounts for an estimated 1.5% of annual U.S. zircon consumption. Zircon demand has spurred increased production and new sources that are expected to now bring about stable supplies and lower prices for the long term future.

Potential for Silica Reclamation-

Fused silica is perhaps the most widely used shell material. It is the major component in many ordinary investment shells and is used in a wide range of particle sizes. Fused silica properties are very advantageous for investment casting. It combines low thermal expansion, good hot deformation resistance and convenient mold knockout and casting clean up. The mixture of fused silica with other shell components is considered a requirement by many investment casters.

Fused silica products are not suitable for reuse in investment shells: Thermal cycles during investment casting cause significant fractions of the amorphous material to crystallize, as cristobalite. Upon cooling, the cristobalite fractures extensively because of an abrupt volume change marking the α - to β -transformation. Reuse of any cristobalite for investment casting, which entails heating through the transformation temperature, would severely weaken the shell.

Incidentally, the presence of fractured crystalline silica can also benefit the reclamation of other mold components. The fractures release the more durable components to some extent, and the fine particles which characterize the fracture products can be eliminated early in the reclamation process with a screen scalping operation.

Recommended Reclamation Processing-

Roll crushing is a suggested comminution method, and is used for this report. Other crushing methods could also be appropriate for reclamation processing. Crushing processes suitable for shell component reclamation needs to break down a friable-matrix mass, but only to the particle size of the grains contained within it, without grinding or breaking them. Roll crushers meet these requirements. They crush by a single impact, with minimal shear and inter-particle attrition. They operate with a constant roll gap setting; this prevents most oversized particles while minimizing undersized particles.

Roll crushing produces several characteristic particle types, descended from the various shell regions. The types are; stucco grains, some with adhering fused silica coatings, zircon (perhaps agglomerated with silica) from the prime layers, silica agglomerations and fine mixed powders.

The concentration of the reusable particles could be accomplished by screening and one of several gravity or dense medium separation methods, depending on scale of the proposed operation and the shell composition.

Screening will remove the fine particles, which are predominantly crystalline silica with some zircon. Gravity concentrators separate components, exploiting the effects on motion arising from differences in specific gravity and particle size. The complexity and efficiency of these separation methods depends on the magnitude of the differences among the various particle categories.

It may be possible to alter composition or practice to accommodate reclamation. For instance, the composition of prime coats refractory could be formulated so that the resulting bulk density does not coincide with the bulk density of aluminosilicate stucco, in order to optimize separations by specific gravity methods. Also, thermal cycles during shell processing could be modified to maximize the crystallization of fused silica, increasing content of microcracked (when cooled) cristobalite, for easy removal of the concomitant fine particles. Although the types of "radical" changes are possible, they are not likely to occur.

CHAPTER ONE

INTRODUCTION-

This report examines the feasibility and methods of investment shell components reclamation. The first part of this report investigates shell compositions and investment practice by means of an industry survey, shell specimen analysis and through the available literature. The required properties of shell components including factors pertinent to component reuse are discussed. The second part of this report reviews mineral processing theory and methods to aid workers with the development of reclamation operations.

Project Background-

The ceramic components of investment casting shells are used for one cycle of shell production and then are discarded. The initial focus of this project was to examine the reclamation of zircon from investment casting shell wastes in order to reduce consumption of this valuable mineral and to conserve landfill space.

Techniques suitable for these goals were sought with literature surveys in the fields of the foundry arts and general ceramics, covering investment casting practice, alternative binder systems, additives to facilitate reclamation and applications from current practice in sand mold reclamation techniques.

To realistically evaluate the potential of zircon reclamation, the Investment Materials Industry Survey was conducted to investigate current shell component material use and related investment practice. Survey results indicated significant difficulties with the originally defined approach- most compositions contained only minor amounts of zircon, restricted to narrow zones of the shell. A large fraction of the zircon was of very fine particle sizes, moreover, the powdered zircon was usually mixed with fine fused silica powders, and entrained within a well sintered silicate-bonded matrix. The balance of a typical shell was fused silica or aluminosilicates, present as powders and a variety of larger grain sizes.

The common shell compositions, required properties and process constraints of the investment casting and the limitations of industrial powder processing capabilities suggested a broader approach to shell reclamation.

Stucco Reclamation-

Several factors indicated a stucco reclamation process could be a useful and achievable goal. From a landfill conservation viewpoint, the stucco is a major volume fraction of the shell wastes generated by casting operations. From an operational economy aspect, reducing consumption of any major component would be beneficial. From the reclamation processing aspect, stucco particle sizes are within the applicability range of many mineral processing methods, giving more options for the reclamation treatments.

Stucco is a tough, stable component that survives the casting process relatively unchanged. Stucco property demands and application methods are more tolerant to the introduction of a recycled product, as opposed to the contamination-sensitive prime coat refractory, where the zircon is employed.

Furthermore, processing methods able to concentrate the stucco could also separate a zircon-rich fraction. The pre-concentration of zircon values could economize the operation of zircon reclamation methods already considered. (Smith, Llewellyn 1985).

CHAPTER TWO

INVESTMENT SHELL PROCESS DESCRIPTION-

The investment casting process [1] (See Figure 1) uses wax patterns mounted to a wax sprue gating system; this assembly is called a tree. The tree is invested with 4 to 14 coats of several ceramic materials. Each coat is applied by dipping the tree into a slurry of binders, refractories and minor additives suspended in a liquid carrier. The dipped tree is withdrawn and allowed to drain. The still-wet layer is stuccoed with larger ceramic particles, applied by inserting the tree into rainfall sanders or a fluidized bed.

The shell is dried after each coat, gelling the colloidal silica binder to cause some strength development in the layer. When sufficient coats have been built up, the wax pattern is melted out in steam autoclaves or in flash fire furnaces, leaving a casting cavity. The shell is then further fired at 1500F - 2200F, which develops a sintered ceramic bond between particles and preheats the mold for metallurgical requirements. The casting is poured and cooled. The mold is knocked off; shell fragments are discarded, either stockpiled on site or disposed of in landfill.

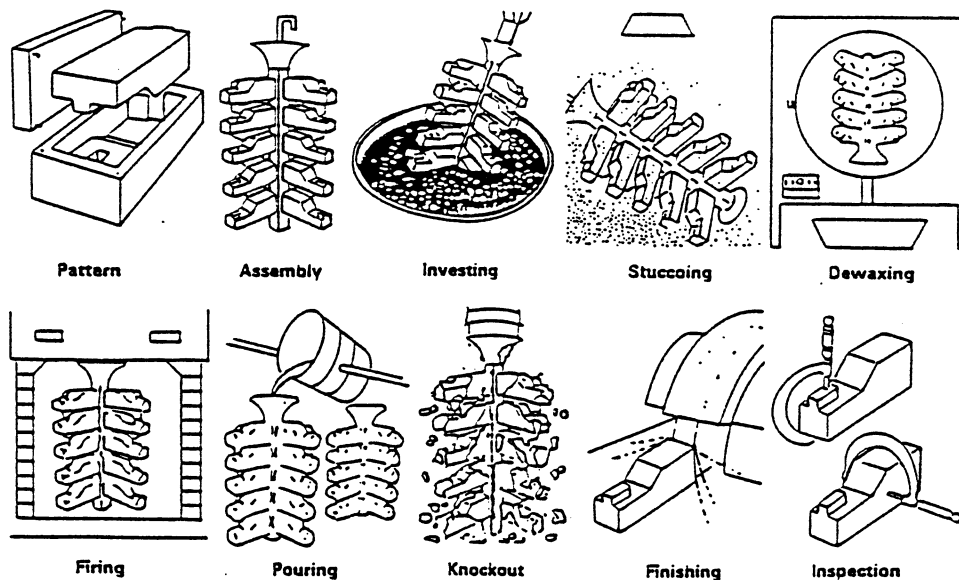


Figure 1. The Investment Casting Process. [1]

Fused Silica-

Fused silica is a synthetic product, produced by carbon arc fusion of high-purity quartz sand followed by quench cooling to retain the amorphous phase. The fused mass is then crushed, and ball milled if necessary, to the desired particle size distributions (see Table 1). Products range from the 4 mesh to below the 325 mesh levels. [2, 3] Fused silica is chemically compatible with common binder systems. It is highly soluble in hot concentrated alkali solutions. Typically >97% amorphous, fused silica is characterized by a relatively low specific gravity of (about 2.2), and a very low and monotonic coefficient of thermal expansion (CTE). It is a poor thermal conductor.

During high temperature thermal cycles, significant fractions of the amorphous fused silica can crystallize, principally to cristobalite. Devitrification begins above about 1800°F and initiates on the particle surface, since most contaminants nucleate the process. [4, 5] Cristobalite exhibits a relatively high CTE compared to fused silica and also undergoes a phase transformation marked with an abrupt volume change that occurs at temperatures within the range of investment casting practice.

Size												
Sieves Mesh	-4+10	-6+50	-10+20	-20+50	-30+50	-50+100	150	-120F	-140F	-200F	-270F	-325F
4	3-18											
6	20-40											
8	20-35	1-7										
10	10-20	6-15										
20	15-30	45-55	80-90	0-1	0-1							
30		10-20	2-15	28-38	22-32							
40		10-20	0-3	35-45	35-45							
50				15-25	15-30	4-10		TR	TR			
80				1-7	2-8		0-1	2-5	1-4	0-0.5		
100						75-85	5-15	2-5	1-4	0-0.5		
140						5-15	20-40	8-12	7-11	1-3	0-1	
200						0-3	20-35	10-15	10-15	3-8	2-4	0-0.5
325							15-30	15-20	15-20	14-19	10-15	2-6
PAN	1-4	6-10	0-1	0-0.5	0-0.5	0-1	8-18	47-53	52-58	73-79	82-86	94-98
ppm Magnetics	0-5	0-10	0-5	0-10	0-10	5-20	100-150	40-80	50-100	20-60	10-40	0-20
Avg. Particle Size*								33-38	29-33	20-24	10-14	8-12

*In microns—is measured by
Cilas Granulometer

Table 1. Fused Silica- Typical Particle Size Ranges.

Zircon-

Zircon is obtained from heavy mineral sand, often as a co-product of rutile and ilmenite sand mining. Zircon sand occurs in narrow particle size distributions and generally rounded grains due to the natural processes producing the deposit. Zircon is used as sand for prime stuccos, or ground to -325 or -200 mesh powders for prime stucco or refractory components. There is a high contact angle between the molten metal and zircon interface. In comparison to fused silica, zircon possesses a high thermal conductivity, low specific heat and high specific gravity. The CTE of zircon is moderately low, nearly monotonic and stable, nearly matching the CTE of mullitic aluminosilicate investment shell components. Zircon has only moderate solubility in hot caustic solutions [6,7,8,0].

The zircon market has been subjected to unusual pressures, resulting in past high costs (See Figure 3) and availability varying to the point of scarcity. Zircon prices were moderate and stable until after 1973, when for a period, virtually all available stocks were placed under contract. The consequent shortage caused large price increases; price slowly declined for several years to near equivalence with pre-shortage prices. The co-product status of zircon has lead to other shortages, during industrial nation recessionary periods, due to decreased demand of the titania primary product. Prices have recently moved upward again. These market conditions have resulted in major new or re-processed sources, soon or now in production, in Australia, the U.S., South Africa and other locations. Authorities now forecast increased stocks and falling prices for the near term and a continuing long term availability. The U.S., historically a significant producer but importer of zircon, has become an estimated net exporter. [10,11]

Past cost and availability problems have excluded many users who once considered zircon based on price, in favor of those users convinced there is no opportunity for substitution. [12] Annual consumption of zircon organized by industry group (See Figure 4) provides some evidence of this.

There are zircon applications, such as for glaze opacifiers (large fraction of "All Other") with suitable substitutes when market price becomes too high. Other major users, (refractories, abrasives, alloy producers) can not substitute in response to price variations. They

instead maintain their consumption level even in high price markets; this indicates the properties unique to zircon are required for the particular application.

This characteristic zircon-consumption behavior has important implications for recycled zircon.

Particle size, size distribution (important physical characteristics) and purity (affects thermodynamic characteristics) are key factors for most price-insensitive zircon consuming industries, and alternative materials not meeting specifications are not acceptable. The grinding and contaminations coincident with investment casting type zircon will likely exclude it from many of these markets.

The large-quantity application of zircon as glaze opacifiers, with a cost & consumption relationship that reveals an option of alternative materials and sources, is however also sensitive to minor contaminations of color producing ions. Such contamination with reclaimed casting mold materials is likely.

In the U.S. consumption, the foundry industry is the largest user of zircon, however the investment casting segment accounts for an estimated 5% of the total foundry consumption [13], or about 1.5% of the annual U.S. consumption. Foundry consumption of zircon sand is prone to substitutes, but use of zircon powder for sand casting mold-wash is less so. One suggested application of reclaimed zircon is as this sand casting mold-wash, which accounts for a large portion of the foundry total. The zircon powders used for this function are similar to investment casting powders. Investment casters who recover a zircon component should attempt trials of the reclaimed, reground material with sand casters.

Significant quantities of zircon are used in the manufacture of zirconia, much of which is intended for the high performance refractory industry. The silica content is removed from the zircon, commonly by alkali decomposition with NaOH above 600°C [36]. Recovered zircon is suitable for this process. The recovered material would include excess amounts of free silica, which could be removed by the caustic leaching method [34] or during the decomposition. Minor level contaminants, (metal residues, mold inoculants, recovery processing contaminants) could have significant effects on the ultimate applications, thus this reuse also requires a detailed qualification test for any specific supplier/user pairing.

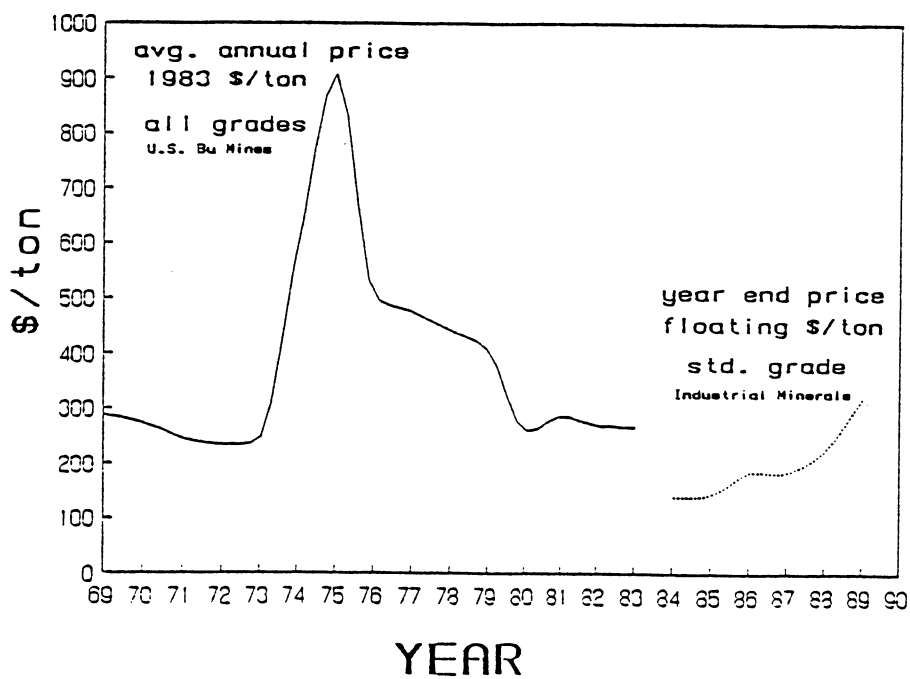


Figure 3. Zircon Time-Price Relationship. [11]
1969-1983, 1984-1989

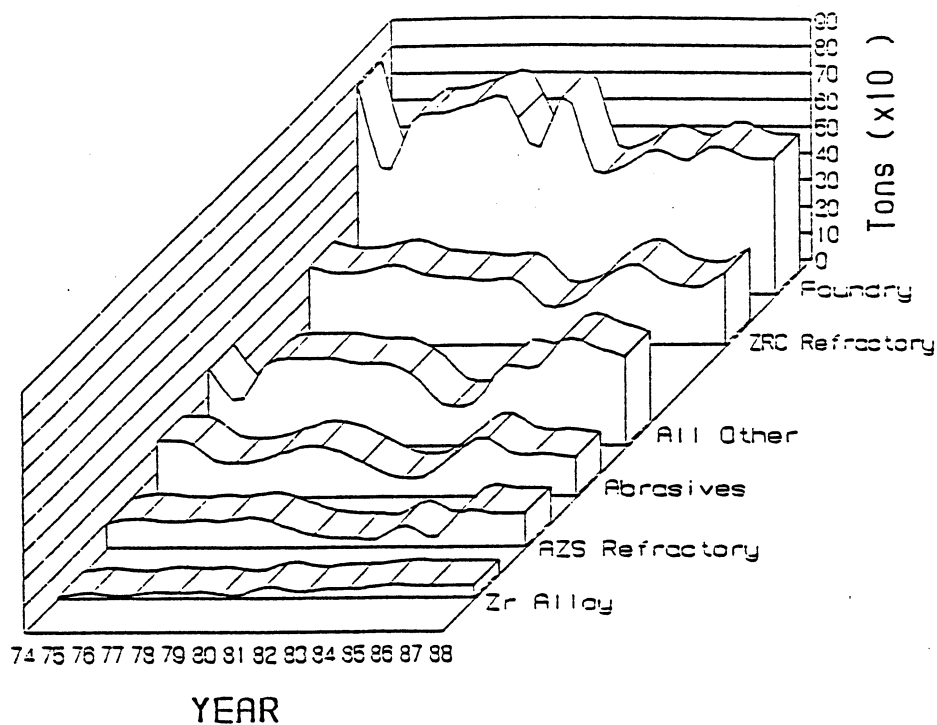


Figure 4. U.S. Zircon Consumption, by Industry.
1974 to 1988. [37]

Aluminosilicate Stuccos-

Aluminosilicate stuccos are produced from fireclay raw materials that are blended, ground, extruded into pellets, calcined at 2600° to 2900°F, then crushed. This process creates grains of interlocked mullite needles and a dispersed silica glass fraction with some cristobalite. Aluminosilicate stuccos are specified according to alumina content, and the higher alumina compositions display generally higher quality properties.

Aluminosilicate stucco is produced in wide ranges of particle sizes and size distributions. (See Table 2). They are available at moderate cost and are chemically and physically compatible with other shell components.

GRADE	SCREEN →														
	8	12	14	16	20	30	40	50	70	100	140	200	270	325	PAN
10x18	0-2	10-16			58-75	8-17									5-9
14x28		0	1 max		30-55	35-45	10-25	5 max							1.5 max
16x30				0-3	65-75		4 max								1 max
22S				Tr	15-25	32-47	27-37	4-10							3 max
35S				Tr	1-5	21-38	40-54		9-19		2-8				3 max
50S					0	1-9	20-34	25-36	15-22	8-13	4-9				3 max
60S						0	0-5	30-48	30-44	9-22	2-7				3 max
20x50				Tr	0-8	20-50		50-72						2 max	Tr
25x80					0-5	Even Distribution		85-98	0-10						2 max
50x100							Tr	5-20		65-86	5-15	3 max			1 max
60x200								0	0-6		58-88	12-25	9 max		1 max
3000	0-2					30-40						18-30			35-45
2001C-C										Tr		15-25			75-85
3251C-C										Tr				15-25	75-85

The flours (2001C-C and 3251C-C) are ground in a ceramic ball mill.

Chemical Analysis		%	%	%
Alumina	- Al_2O_3	47.8	58.0	68.0
Silica	- SiO_2	49.3	38.3	27.9
Titania	- TiO_2	1.78	2.25	2.61
Ferric Oxide	- Fe_2O_3	0.98	1.31	1.33
Calcium Oxide	- CaO	0.03	0.04	0.06
Magnesium Oxide	- MgO	0.04	0.05	0.04
Sodium Oxide	- Na_2O	0.04	0.02	0.03
Potassium Oxide	- K_2O	0.03	0.03	0.03
Specific Gravity,	(Gm/cc)	2.64	2.80	2.85
PCE		34	37	39

Table 2. Aluminosilicate Stucco Products.

Colloidal Silica Binder-

Colloidal silica is the most prevalent shell binder in U.S. investment foundries. Colloidal silica offers good strength, economy, availability, environmental safety and stability with correct use. Investment casting type colloidal silica dispersions are amorphous silica particles with diameters from 4 to 40 nM., which relates to surface areas of hundreds of $M^2/gm.(SiO_2)$.

Colloidal silica acts as a cement. Drying to remove free water forces silica particles together until capillary effects overcome surface charge repulsion. Silanol ($-\text{Si}-\text{O}-\text{H}-\text{O}-\text{Si}-$) bonds form between particles which provide mold green strengths on the order of several hundred PSI (MOR). Heating to 400°F removes most combined water, converting the silanol bonds to siloxane ($\text{Si}-\text{O}-\text{Si}$) bonds. Complete reaction and highest mold strength, on the order of several thousand PSI (MOR) comes after sintering at temperatures $>1400^{\circ}\text{F}$. [14,15,16]

Colloidal silica dispersions are most stable when maintained at 8.5 to 10.5 pH, which prevents particle aggregation by maintaining negative surface charges. Low contents of ionizable cations can irreversibly gel colloidal silica by neutralizing the surface charge. (See Figure 5)

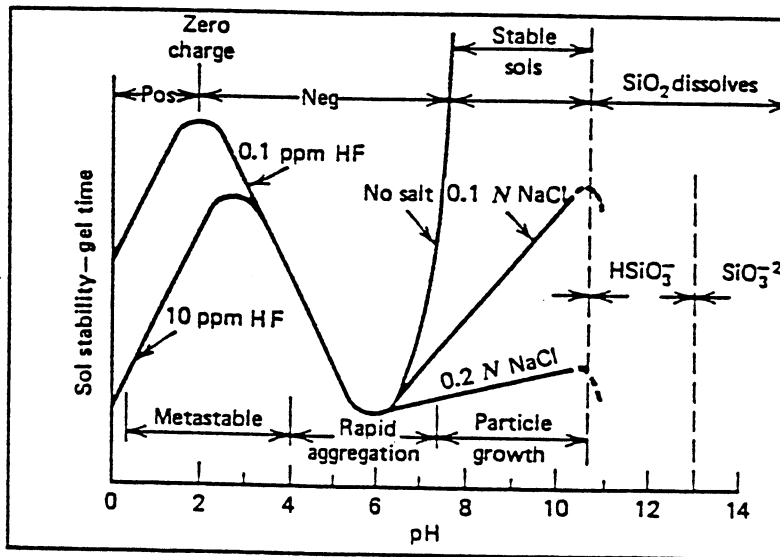


Figure 5. Effect on Stability of pH and Ionic Content in the Colloidal Silica-Water System.

Material Economic Analysis

The investment casting survey which was conducted as part of this investigation estimated that an average of 1.18×10^6 pounds of investment waste shell is disposed of annually per foundry. A 1990 AFS survey estimates that there are approximately 300 investment casting foundries. Therefore, it is estimated that over 354 million pounds of investment shell material is disposed of annually in the United States. This translates to 177,000 tons per year. A 1991 AFS research report on foundry waste estimates that average disposal at \$45/ton. Therefore, the investment casting industry is estimated to spend approximately \$8 Million for disposal of their spent investment casting shell materials. The average investment foundry spends about \$250,000 annually on shell materials and disposal costs.

This report summarizes the various techniques which could be used to reclaim spent investment shell material. It further attempts to describe the procedures which could be used to separate the aggregates (i.e., zircon, silica) of the shell into their respective fractions.

It is beyond the scope of this investigation to predict the actual costs to reclaim the investment shell for reuse. However, we have summarized the average cost to buy the raw materials for the average shell and the cost to dispose of the spent shell. This summary is as follows:

Average Foundry (Without Reclaim)

Typical I.C. Shell	\$/Ton	Tons Annually	\$/Year
5% Zircon	600.00	30	18,000
30% Silica	360.00	177	63,720
65% Alumina-Silicate	360.00	383	<u>137,880</u>
		Subtotal	219,600
Solid Disposal	45.00	590	26,550
		Total	246,150
		Total (\$/Ton)	- 417.20

Average Foundry (With Reclaim)

Typical I.C. Shell	\$/Ton	Tons Annually	\$/Year		
5% Zircon	600.00	30	18,000		
20% Silica	360.00	118	42,480		
75% Reclaim	***	442	***		
Solid Disposal at 10%	45.00	59	2,655		

Total - 246,150

Total (\$/Ton) - 417.20

*** These numbers would be worked backwards through the average/ton costs of shell without reclaim.

Therefore, if reclaim costs (including capital and operating costs) are \$310/Ton or less, then it would be economical for the foundry to consider shell reclamation.

CHAPTER FOUR

MATERIALS FACTORS OF INVESTMENT CASTING SHELLS-

Although ceramics account for perhaps only 5% of the total costs of a casting, mold quality greatly influences casting quality and overall operation economy. [17]

Some required properties of investment shells, the materials used (introduced in the previous section) and how they satisfy those requirements, with some factors relevant to reclamation or reuse of those materials are discussed.

Investment shells are well developed, complex composites and certain changes to composition or practice are not plausible. While the constraints on investment shells must be respected, understanding the interrelated materials factors will then allow certain reclamation facilitating modifications to be considered.

Prime Refractories-

Finely ground powders of fused silica and zircon, or mixtures of the two are the common prime refractories. Since refractories of the first prime coat provide the mold-to-metal interface, these components must perform critical functions.

Prime Refractories- Fused Silica

Ground fused silica is the most prevalent prime refractory component, due to its excellent service characteristics. Its very low CTE increases thermal shock resistance and maintains dimensional stability of molds.

Cleaning of castings is simplified by the inclusion of fused silica. Mold knockout operations are aided by cristobalite formation and the associated shell weakening resulting from microcracking developed during the volume changes of the α - to β - transformation. Final cleaning of castings in hot sodium hydroxide is possible due to the high solubility of any adherent silica.

The low density of fused silica confers less obvious benefits of more shell material per purchased weight; and lighter shells with lower handling stresses can be thinner than shells fabricated of denser materials.

There are certain drawbacks associated with the use of fused silica. The low thermal diffusivity of fused silica may adversely affect metal microstructures.

Reactions between silica and some liquid metals or their oxides can cause casting defects. [18,19] Cracking of cristobalite prevents the cool storage of fired molds.

The disadvantages of fused silica are countered, where necessary, with a zircon component.

Prime Refractories- Zircon

Zircon's low reactivity with molten metals inhibits many mold-originated casting defects, particularly with reactive aluminum and magnesium alloys or at the high temperatures of iron casting. The high thermal diffusivity of zircon can chill solidifying castings for improved microstructures.

Zircon is stable at temperatures experienced during investment casting and undergoes no weakening phase transformations upon cooling. The retained strength of high-zircon shells may interfere with casting knockout operations. High levels of zircon, which is only moderately soluble in hot caustic solutions, can contribute to difficulty in cleaning intricately detailed castings.

Prime Refractories- Mixtures.

Zircon is the sole prime coat refractory component at some investment foundries; pure fused silica is employed at many foundries. However, most foundries opt for a mixture of zircon and fused silica. Molten metal and casting problems demand the zircon prime component, but efficient shell removal requires the weak link of a crystallized silica fraction.

Particle Size and Surface Finish.

The desirable surface detail and finish possible in investment cast articles is imparted by the mold surface, which is limited by the particle size of the prime coat refractory. The finely ground powders required are specified as -200 or -325 mesh, but are predominantly much smaller, with many particles extending even into the colloidal size range. [21]

Prime Stuccos-

The first prime stucco should be small, rounded particles, to avoid penetrating the thin prime layer while supporting surface detail and recesses, [23] and to form dense layers which resist metal penetration.

There are usually two prime stucco coats applied. The first prime stucco is most commonly pure zircon sand or powder, and less often fused silica. Second prime stuccos are zircon sand or powder, zircon / fused silica mixtures, pure fused silica or zircon aluminosilicate mixtures. Prime stucco (perhaps the main use of zircon) represents only a small volume fraction of a shell even if both stucco coats are zircon only. Due to the small particle size of prime refractory, the prime stucco is entrapped in a well sintered matrix.

Backup Coat Functions-

Perhaps the main requirement of investment shells is sufficient strength. Dried shell strength must be high enough to withstand stresses of mold handling and forces due to thermal expansion mismatch during mold drying and pattern melt out. A fired strength 2 to 5 times higher than dried strength levels is developed to resist breakage and deformation from the thermal shock, erosion and metallostatic pressures during pouring. [27]

The force required to break a shell is a function of both shell composite MOR value- M and thickness- d . Rearranging the MOR formula and neglecting constant terms, the breaking force- W is;

$$W = d^2 \cdot M \quad \text{Eqn. 1}$$

Coarse particles, such as stucco, actually lower MOR values compared to fine refractory powders. However, the quadratic exponent on the thickness term dominates the breaking force expression; since coarser stucco builds the most thickness with a given number of dipped coats, this provides the most economical production rates.

Backup Refractories-

Backup refractories are most commonly fused silica in the size range of fine sand. Use of zircon refractory in the backup layers is very exceptional; since backup refractory will not interact with liquid metal there is little incentive to use zircon. Aluminosilicate powder backup refractory is reported in some applications, sometimes obtained as a recycled product.

Backup Stuccos-

Backup stuccos are coarse particles of fused silica or aluminosilicates.

Aluminosilicate stucco is often used, offering sufficient properties at a lower cost than fused silica. These compositions are more refractory and also are stable during investment casting thermal cycles. The ratio of mullite to glass is fixed by the overall alumina content and the glass fraction is stabilized and reinforced by the highly distributed mullite particles. There is a cristobalite content reported in the lower alumina grade stuccos, but no information on a related thermally induced stucco degradation was found.

Narrow particle size distributions of stuccos are required to reduce particle size segregation in fluid bed applicators. Dust levels should be minimal to allow good stucco adhesion onto the wet dip.[25]

Eight percent of the 700 tons of annual fireclay production in the U.S. is used for foundry sands, but the fraction of this destined for investment casting is not reported. Recycling efforts for this material as a class are described as currently insignificant, but greater recovery of by-products and co-products of clays are anticipated due to solid waste disposal issues. [26]

Binders-

Colloidal silica is an excellent investment casting binder, and dominates the U.S. industry. Colloidal silica is refractory enough to permit high temperature preheating to facilitate mold filling of complex, thin wall castings. Metallostatic pressures could cause strain in excess liquid contents due to any less refractory binders, which would degrade dimensional tolerances.

Colloidal silica slurries are destabilized by electrolyte contamination. Fairly low concentrations of ionizable cations can irreversibly gel the colloidal dispersion. Gelation degrades mold strength and causes defects, which may be difficult to detect at a convenient stage. Slurry contamination requires discarding the entire slurry, which would negate the economy of recycling. Reclamation processing residues, cast metals or grain refining agent contaminants will be foundry-specific. The control of these will be a difficult challenge to the investment casting reuse of zircon.

CHAPTER FIVE

INVESTMENT MATERIALS INDUSTRY SURVEY-

Survey Introduction-

An industry survey was conducted to obtain information on representative investment shell compositions. The survey solicited the investment practice which determines component distribution in shells and estimates of waste quantity generation.

Summary of Survey Results-

Prime refractory compositions are pure zircon, mixed zircon-fused silica, and pure fused silica, reported about equally.

Prime stuccos are usually zircon sand or powder.

Backup refractories are predominantly fused silica.

Backup stuccoes reported are evenly divided between aluminosilicate and fused silica grains.

Waste shell generation reports are extrapolated to annual quantities. Output estimates ranged from 100,000 lbs./year, to 4,000,000 lbs./ year.

Survey Distribution And Participation-

Surveys were distributed to ninety U.S. and Canadian investment casting foundry members listed in the Investment Casting Institute directory. Twenty five foundries returned responses. Sixteen of these returned detailed information for the survey. Three declined to give detailed responses due to proprietary reasons. Six declined to give detailed responses, indicating only that no zircon was used. Foundry identification is withheld per agreement with respondents.

The survey responses are compiled in Table 3- Prime Coat Compositions and Table 4- Backup Coat Compositions. The tables organize components into refractory, stucco and binder categories by individual coats. The relative weights of mixed refractory or stucco components are given as decimal fractions. In Table 4- Backup Coat Compositions, where several successive layers are identical, coat numbers are used to condense the information. Single foundries employing more than one composition (usually variations of prime coat refractory mixture) are given numeric suffixes.

Table 3. Prime Coat Compositions.
Investment Materials Industry Survey.

FIRM	FIRST REFRACTORY SLUICE	PRIME SLUICE	COAL BLINDER	SECOND REFRACTORY SLUICE	PRIME SLUICE	COAL BLINDER	MOORE PRIME?	FIRM
A	2200 1.00 298	2200 1.00 298	LP30, M1030	2200 1.00 298	2200 1.00 298	LP30, M1030	NO	A
B	2325 1.00 2100	2325 1.00 2100	RRPC	2325 1.00 2100	2100	RRPC	NO	B
C	2200 1.00 1550/100	2200 1.00 1550/100	RRPC	2200 1.00 1550/100	1550/100	RRPC	NO	C
D-1	2200 1.00 2120	2200 1.00 2120	M6001	2200 1.00 2120	2120	M1030	NO	D
D-2	2200 1.00 1550/100	2200 1.00 1550/100	M6001	2200 1.00 1550/100	1550/100	M1030	NO	E
E	2325 1.00 2120	2325 1.00 2120	LP30	2325 1.00 2120	2120	LP30	NO	F
F-1	2200 0.80 290/105	2200 0.80 290/105	M6001	2200 0.80 290/105	290/105	LP40	NO	G
F-2	2200 0.80 290/105	2200 0.80 290/105	M6001	2200 0.80 290/105	290/105	LP40	NO	H
G-1	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	I
G-2	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	J
G-3	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	K
G-4	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	L
H-1	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	M
H-2	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	N
I	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	O
J	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	P
K-1	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	Q
K-2	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	R
L	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	S
M	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	T
N	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	U
O	2200 1.00 2120	2200 1.00 2120	LP30	2200 1.00 2120	2120	LP30	NO	V

Table 4. Backup Coat Compositions.

FIRM	BACKUP COAT	PRIME SLUICE	COAL BLINDER	SECOND REFRACTORY SLUICE	PRIME SLUICE	COAL BLINDER	MOORE PRIME?	FIRM
A	2200 1.00 298	2200 1.00 298	LP30, M1030	2200 1.00 298	2200 1.00 298	LP30, M1030	NO	A
B	2325 1.00 2100	2325 1.00 2100	RRPC	2325 1.00 2100	2100	RRPC	NO	B
C	2200 1.00 1550/100	2200 1.00 1550/100	RRPC	2200 1.00 1550/100	1550/100	RRPC	NO	C
D-1	2200 1.00 2120	2200 1.00 2120	M6001	2200 1.00 2120	2120	M1030	NO	D
D-2	2200 1.00 1550/100	2200 1.00 1550/100	M6001	2200 1.00 1550/100	1550/100	M1030	NO	E
E	2325 1.00 2120	2325 1.00 2120	LP30	2325 1.00 2120	2120	LP30	NO	F
F-1	2200 0.80 290/105	2200 0.80 290/105	M6001	2200 0.80 290/105	290/105	LP40	NO	G
F-2	2200 0.80 290/105	2200 0.80 290/105	M6001	2200 0.80 290/105	290/105	LP40	NO	H
G-1	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	I
G-2	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	J
G-3	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	K
G-4	2325 1.00 2120	2325 1.00 2120	M1130	2325 1.00 2120	2120	M1130	NO	L
H-1	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	M
H-2	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	N
I	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	O
J	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	P
K-1	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	Q
K-2	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	R
L	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	S
M	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	T
N	2200 0.75 2200	2200 0.75 2200	LP30	2200 0.75 2200	2200	LP30	NO	U
O	2200 1.00 2120	2200 1.00 2120	LP30	2200 1.00 2120	2120	LP30	NO	V

The tables are organized in descending order of zircon fraction in the prime coat slurry. This will not exactly indicate zircon consumption quantity or rate, nor suggest feasibility of zircon reclamation for any particular foundry, due to the other shell practice variables.

Survey Responses

Prime Coat Refractories-

Eight of the responding foundries mix fused silica and zircon refractory components in the prime coat slurries. Six of the responding foundries use only ground zircon. One responding foundry and presumably the six "no zircon" respondents use only ground fused silica refractory.

Zircon refractory components are employed only in the prime coats (with one exception). Moreover, seven foundries eliminate or reduce the zircon refractory after the first prime coat, replacing it with fused silica.

Prime Stucco-

Prime stucco, with few exceptions, is zircon sand or ground zircon. Fused silica is reported three times and an aluminosilicate mixture with zircon is reported once. Most foundries maintain the use of zircon stucco for the first and second prime coats, but substitutions of fused silica grain in the second prime stucco are reported.

Backup Refractories-

Backup refractory is fused silica, with very few exceptions; one foundry uses zircon throughout the shell, and one foundry (that also omits the second prime) uses an aluminosilicate powder for refractory.

Backup Stucco-

The backup stucco compositions reported are evenly divided between aluminosilicates and fused silica. The only variation in subsequent coats may be to a larger particle size of a similar composition.

Survey Limitations-

This survey did not request information on relative consumption rates of each raw material. This valuable factor was not solicited in order to encourage responses to the survey; earlier discussions with several foundry representatives indicated this information could be considered business sensitive. Neither were true quantitative bulk compositions of shells obtained from the survey responses. The investment procedure of repeated dip and stucco cycles causes variations in the distribution of refractory and stucco components. The overall composition can be estimated by either modal analysis of cross sections or a method demonstrated for this report which correlates energy dispersion chemical analysis line scans (SEM-EDS) with X-ray diffraction (XRD) phase identification. See section on Shell Phase Compositions.

This survey may not accurately represent shell compositions across the entire industry, so estimates of industry-wide material consumption using these results is not attempted. The specific reference to zircon reclamation in the survey announcement probably skewed the response toward zircon-using foundries, resulting in an overrepresentation of such compositions, while fused silica users had less incentive to respond. This is indicated by the six foundries who at least responded "no zircon used". These six foundries, presumably using fused silica primes with fused silica or aluminosilicate stucco, are not represented in the tables.

CHAPTER SIX

SHELL PHASE COMPOSITIONS-

The composition of several representative shells were analyzed by combining XRD phase analysis with SEM-EDS standardless chemical analysis.

A Phase Distribution graph displays the result on shells of the alternating dip/stucco construction procedure. This has a significant effect on reclamation; for example, the limited zones of zircon use explains the necessity of a preconcentration step before final recovery is attempted.

A Phase Composition graph has been prepared from four representative shells to portray compositions to be dealt with in recovery. It can be seen that the overall zircon component is very limited in most shells, the aluminosilicate (mullitic) materials are much more prevalent and silica will be a large factor in all shells reported in the Industry Survey.

Phase Distribution Graph-

A phase distribution graph (See Figure 6) indicates the composition zoning that all shells with multiple components display. It is also a method to estimate the overall composition shell waste. The phase distribution within the shell is included for a representative specimen obtained with the Shell Materials Industry Survey.

Phase distribution graphs could also measure shell construction processes, as indicated by homogeneity of components distribution. A well distributed assembly of the several components would optimize the use of shell materials and improve shell performance. The capability to do this evidently varied greatly from foundry to foundry.

The method used for this graph correlates SEM-EDS (standardless) chemical composition analysis at known positions in the shell to the bulk phases identified by a X-ray diffraction (XRD) analysis. The elemental composition analysis obtained at each linescan was then converted to ratios of the associated compounds, and plotted.

Method

The SEM-EDS chemical analysis is obtained from 10mm length linescans on a polished cross-section of a shell, scanned parallel to the mold face, progressing through the layers at selected intervals. The elemental quantities from EDS analysis are converted to corresponding oxide mol fractions. The oxide mol fractions are related to the compounds identified with XRD, in the following manner; Aluminum content is present only in mullite; therefore, all aluminum measured by the EDS analysis is assumed to be a constituent of mullite ($3\text{-Al}_2\text{O}_3 \cdot 2\text{-SiO}_2$), and the appropriate ratio of silicon is deducted from the total silicon measured by EDS. Similarly, all zirconium indicated by EDS analysis is present only as zircon (ZrSiO_4), so all zirconium content is assigned to zircon and the corresponding silicon is subtracted from the total silicon. The balance of the silicon is both crystalline and amorphous silicon oxide, and is designated only as silica content. The compounds are then calculated as weight fractions of the composition for each linescan. This data is plotted, with component weight fraction on the ordinate, and position within shell (of the line scan) on the abscissa.

This Phase Distribution Graph was produced from Specimen L. The prime coats lie to the left, where the zircon content is highest. The variation in zircon level seen on the graph reveals the location of the two prime refractory dips and the two prime stucco layers. This prime refractory comprises 50/50 mixtures of fused silica and zircon prime refractory, and the prime stucco is a 50/50 mullite and zircon mixture. The backup coats comprises fused silica refractory and aluminosilicate stucco.

The phase distribution in shell "L" (Figure 6) is presented. The far left side of the chart represents the mold/metal interface. Moving to the right on the graph shows the relative amount of the various phases throughout the mold in-situ, which result from the individual investment layers.

The zircon (dark stripe area) in the prime coat zones occurs as refractory (most of the zircon area) and first and second stuccos (the peaks in the zircon area).

The silica (light stripe area), added with the prime refractory mixtures, the refractory in the backup coat slurry, and colloidal silica binder is seen throughout the shell in varying amounts.

The mullite (white area) shows the distribution of the mullitic prime stuccos (which was mixed with zircon), increasing into the backup zones when the stucco type is changed. The peaks in the mullite backup coat zone are the stuccoed layers.

APPROXIMATE PHASE DISTRIBUTIONS

SPECIMEN L
by SEM linescan (100X) and XRD data

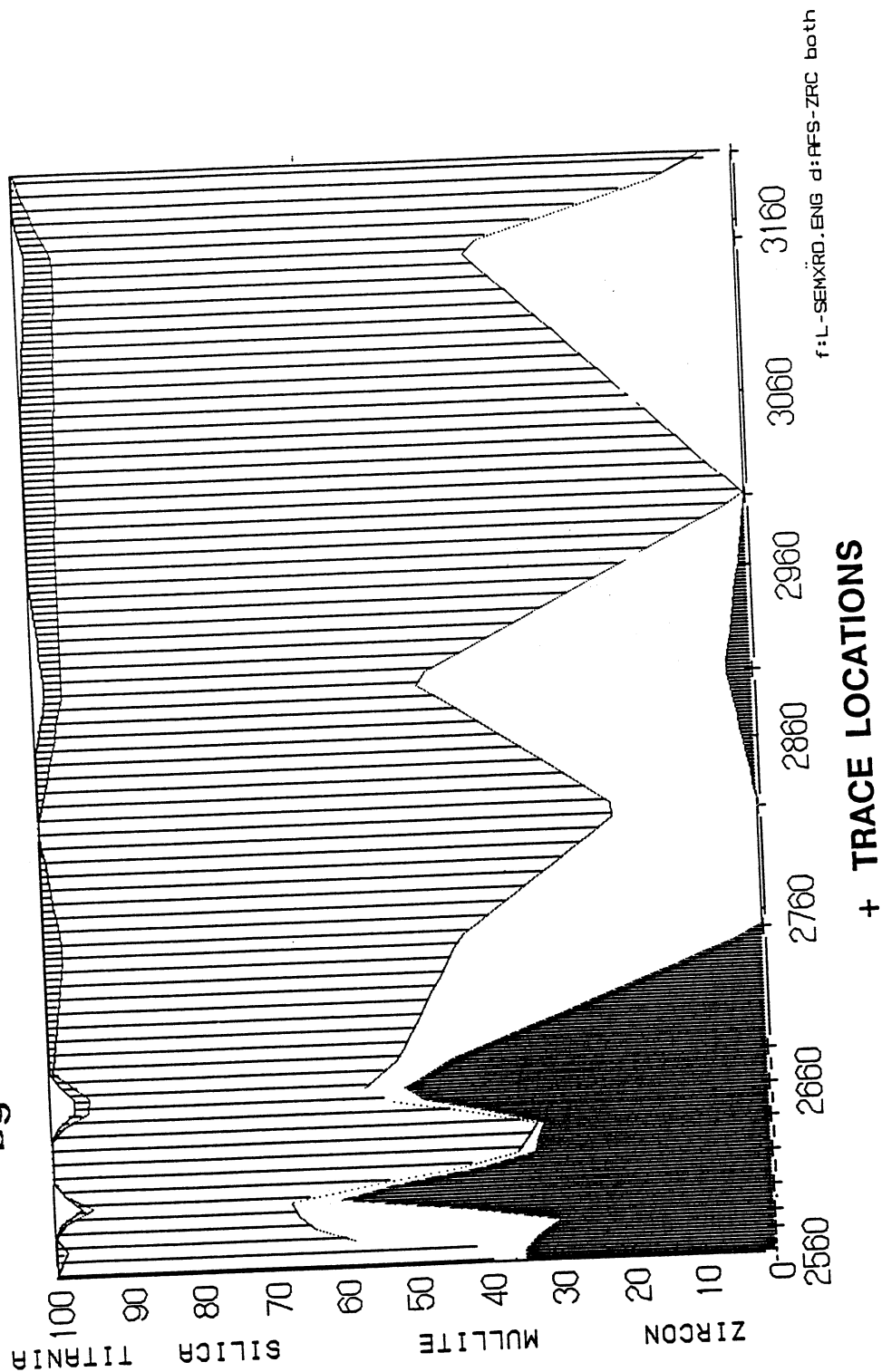


Figure 6. Phase Distribution Graph

The Phase Composition (See Figure 7) was determined for four shell compositions that represent major categories reported to the Investment Materials Industry Survey. The phase data for the graph was obtained by a similar method to the Phase Distribution Graph- elemental compositions indicated by SEM related to the phases indicated by XRD analysis.

The specimens for analysis were finely ground shell material. For each shell, enough material was analyzed to ensure an accurate representation of the composition. Approximately 200 gm. samples of each shell specimen graphed was ground in a ring pulverizer to pass a 325 mesh screen, riffle split to reduce volume and pressed into a specimen mount. A SEM-EDS analysis was measured on a 1 mm. by 1 mm. square of the pressed mount. Another fraction split from the pulverized specimen was examined by XRD phase analysis.

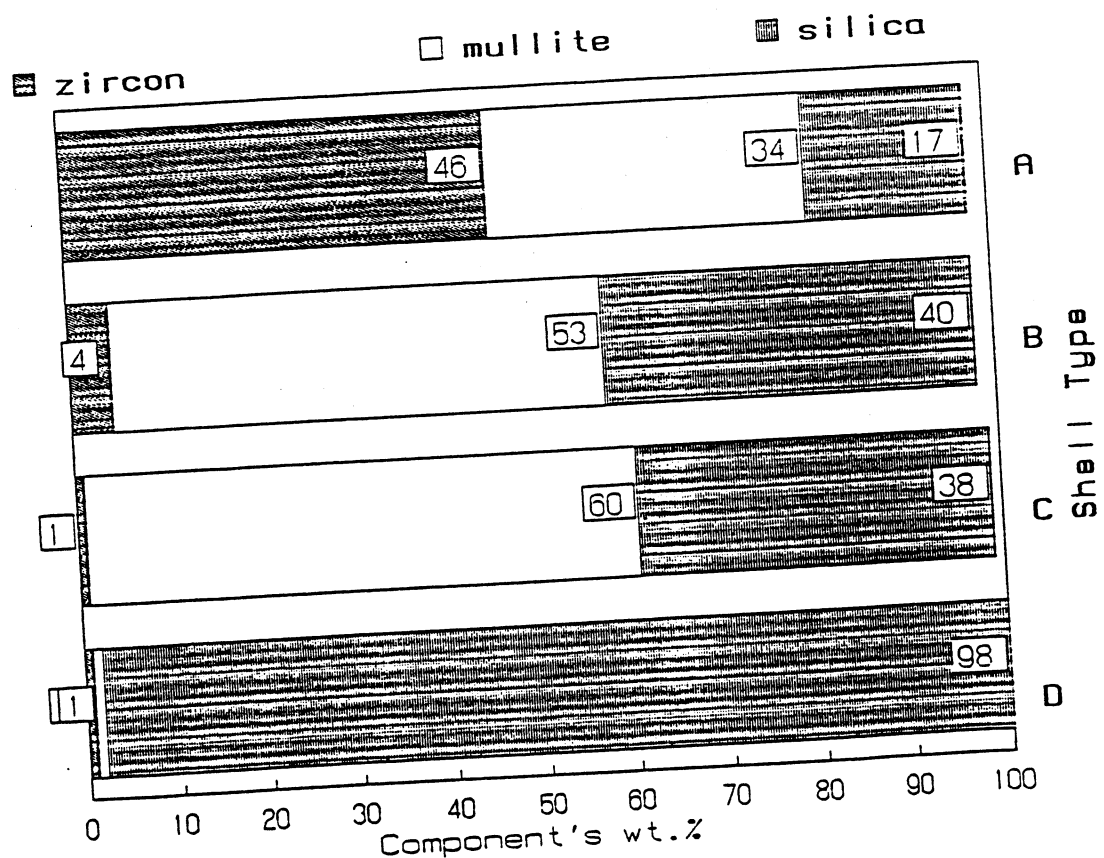


Figure 7. Overall Phase Composition.

CHAPTER SEVEN

LITERATURE SURVEY-

Investment Shell Reclamation Operation-

Shell component reclamation is practiced at the Howmet Turbine Components Corp. [33] A two stage crushing with an intermediate screen separation produces zircon flour and alumina grains, this distribution resulting because of differences in friability. The zircon flour is separated using air current classification and screened at the 325 mesh level. The +325 mesh material is reused in the refractory slurry. The -325 mesh material is not reusable for the investment process, and is disposed of. The alumina (80-85% pure) fraction is screened at 40 mesh, and the +40 mesh fraction is reused as backup stucco, and the -40 mesh fraction is disposed of.

The Howmet investment shell composition indicated by specifications for the reclaimed fractions is unusual, due to the specialized castings produced there. There are relatively low levels of silica present in comparison to typical Investment Shell Materials Survey compositions, and Al_2O_3 (as alumina) is present. No specific shell composition or zircon percentage has been reported by Howmet. The alumina component and the low silica level are favorable to reclamation economy.

Zircon Reclamation Method Studies-

The recovery of zircon from used investment casting molds was investigated by Smith and Llewellyn. [34] One steel foundry and two aerospace casting shells were used in the investigation. The zircon composed 22, 44 and 60 percent of the three shell systems analyzed. The remainder of the three systems contained mullite and silica.

Liberation Methods-

Liberation methods employing rod mill grinding, autogenous attrition grinding and caustic leaching were studied. Rod milling left the zircon surfaces with adherent silica binder which prevented subsequent separation with the flotation agents used. Attrition milling cleaned the surface, but damaged the zircon, causing a 26%-40% zircon loss in the -400 mesh fractions that were considered unrecoverable. Caustic leaching rendered clean zircon surfaces with reagent consumption rates of 300 lb. NaOH / ton (shell), but the accompanying sodium contamination suppressed the flotation agents used for separation, even after several rinses.

Separation-

Separation of zircon from other shell components was attempted by the methods of flotation, mineral table gravity separation, caustic leaching and screen sizing.

Flotation experiments proved cocamine acetate a successful collector; however, the experiment employed synthetic shell-duplicating mixtures of virgin materials. This implies material without a realistic surface coating, which may affect flotation "identity".

Mineral tabling [38] may be an appropriate concentration technique. Shells were ground in rod mills and sized at the 100, 150, 200 and 400 mesh levels prior to tabling. The recombined size fractions of concentrates contained 86.7% zircon for a 61.2% recovery. Further upgrade to 90.8% zircon concentration was accomplished by caustic leaching, (one hour, 160° C, 300 lbs. NaOH /ton) with <1% additional zircon loss. The concentrate was then upgraded even further to 98.6% zircon with a magnetic separation. Overall zircon recovery for combined tabling, leaching and magnetic separation was 57%.

Caustic leaching yielded a concentrate of 98% purity for an 81% recovery, requiring 300 lb. NaOH / ton shell to adequately remove the adherent silica. The shell used for the caustic leaching had high initial zircon contents of 60% and 44% and low initial silica contents of 18% and 0%. This is an unusually low silica level compared to shell compositions reported in this report.

Foundry Mold Reclamation Process-

Extensive information [35] exists on methods used to reclaim sand mold materials. The typical reclamation process begins when the heat from the solidifying casting burns, dries, or otherwise weakens the binder phase; then mold shakeout, breakup of large lumps, perhaps further burn out of mold binders, and air flotation removal of excess fines from degraded mold components is performed. The sand is reconditioned with empirically determined additions of new sand and binders for consistent mold performance.

The problems inherent in reclaiming investment shell materials are very different from those experienced in the reclamation processes common for sand mold materials.

The ceramic bond between particles from the colloidal silica binder is much stronger and more durable than the sodium silicate, clay and water or organic bonds of other sand casting techniques. Also, the thermal cycles during investment casting processes developed a sintered bond. These facts remove investment shell reclamation from the foundry arts into the mineral processing field.

CHAPTER EIGHT

MINERAL PROCESSING FOR RECLAMATION-

The fundamental operations of mineral processing are;
(1) liberation of the values from the gangue
(2) separation of the values from the gangue.

A shell fragment is comparable to an ore fragment. Shells consist of values; zircon and aluminosilicates, intergrown to various degrees with the gangue; silica, which is to be discarded. Comminution treatments are required to liberate the values, and will produce a range of identifiable fragments. (Figure 8)

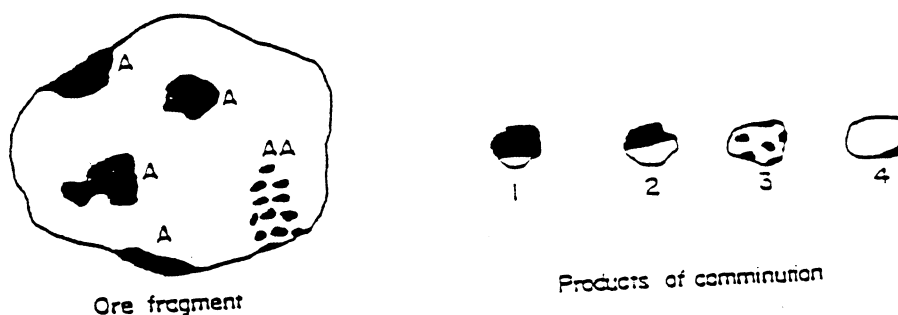


Figure 8. Ore Fragment and Products of Comminution.
1-concentrate, 2,3-middlings, 4-tailings.[38]

The reclamation of investment shell wastes begins with liberating the component particles from the shell. A completely successful liberation would yield the original stucco particles, in the original particle size ranges, free from silica contamination. Comminution processes which entail a minimum of grinding will preserve the size and shape of the particles. Roll crushing appears to meet these restrictions.

Crushing-

There are several types of crushers used for mineral processing; jaw, gyratory and roller units. Roller crushing will be discussed after some criticism of the other crusher types.

Jaw crushers [39] are primary crushers producing coarse particles, and cannot produce small particles in narrow size distributions, due to operation by jaw swinging.

However, a preliminary reduction of shell material using a jaw crusher would confer several advantages. Reducing the largest shell fragments will help to control the feeding rate into the secondary crusher. Also, significant amounts of crystalline silica that fractured to fine particle sizes, released by simply jaw crushing, can be screened out while the majority of particles are still relatively coarse. This reduces secondary crusher capacity requirements and eliminates troublesome fines.

Gyratory crushers are principally very high capacity units. [40] A smaller, specialized type of gyratory crusher, the gyradisc crusher [41], is used in the quarry industry for sand and gravel production, a task not unlike stucco production. These units can operate at appropriate particle size ranges for investment casting stuccos, and the particle-particle contact may serve to scrub the stucco surface free of adhering silica. It may also have the undesirable effect of damaging and rounding the stucco. A gyradisc crusher was not available for this investigation, but these units should be tested for investment shell reclamation operations.

Roll Crushing-

Roll crushers were used for the comminution of investment shell materials in this investigation.

Roll crushers [42] are used where friable, sticky, low abrasion feeds would tend to choke the higher capacity jaw or gyratory crushers. Crushing occurs with one application of pressure, rather than a progressive reduction. The gap set (the distance between the rolls) limits the particle size exiting the crusher when operated with the "starvation" feeding rates that reduce yielding of the spring-mounted rolls. The single crushing event, lacking interparticle contacts-under-load, limits grinding and attrition.

The disadvantage of roll crushers are the limited particle reduction ratios possible. A particle must be gripped to be crushed, which either limits the maximum size of the fragments fed to the crusher or requires large diameter rolls. This may not be an objection with investment shell material feedstocks, since the plate-like fragments already have one small dimension.

Roll Crushers, Parameters and Theory-

Consider a spherical particle of radius- r , to be crushed by a set of rolls with compressive force- C , radius- R , a roll gap- $2a$, coefficient of friction- μ , and the angle of nip - θ , formed by the tangents to the rolls at their contact points with the particle. The roll geometry model is (See Figure 9) [42]

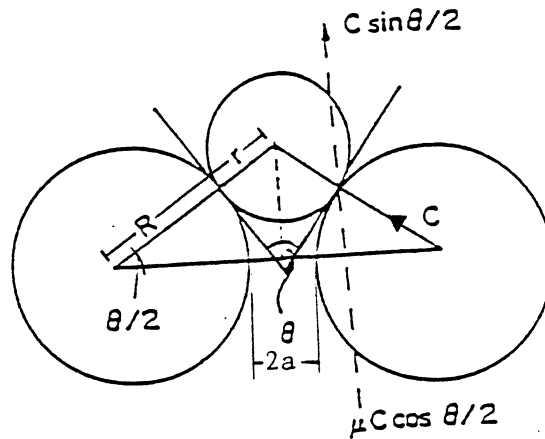


Figure 9. Roll Geometry.[42]

For a particle to be just gripped by rolls,

$$C \sin \theta/2 = \mu \cdot C \cdot \cos \theta/2 \quad \text{Eqn. 2}$$

or

$$\mu = \tan \theta/2 \quad \text{Eqn. 3}$$

Also using Figure 9, the maximum size particle that can be crushed, related to the roll diameter and the reduction ratio (R/a) desired is

$$\cos \theta/2 = \left[\frac{R + a}{R + r} \right] \quad \text{Eqn. 4}$$

The coefficient of friction between many minerals and steel is on the order of 0.2 to 0.3, therefore the angle of nip should not exceed 30°.

Rolls speeds are typically 1 m/s for small rolls of 0.2 m. diameter, up to 15 m/s for large rolls of 2 m diameter. The kinetic coefficient of friction- (μ_k) will decrease with increasing roller speed- (v) (m^0s^{-1}), and can be estimated with

$$\mu_k = \left[\frac{1 + 1.2 v}{1 + 6 v} \right] \cdot \mu \quad \text{Eqn. 5}$$

The theoretical capacity of a roll crusher can be estimated by assuming a ribbon of material passes through the space between the rolls at the roller's velocity. Using the roll speed- N (rpm), roll diameter- D (m), roll width- W (m), roll gap- $2a$, and the specific gravity of the feed material is- σ ($kg./m^3$), the capacity- C is,

$$C = (188.5) \cdot N \cdot D \cdot W \cdot \sigma \cdot 2a \quad kg./hr. \quad \text{Eqn. 6}$$

Realistic feeding rates, inter-particle voids and efficiency losses in particle gripping affect the actual capacity, which can be 25% or more of the theoretical capacity.

CHAPTER NINE

CRUSHING TRIALS-

Method-

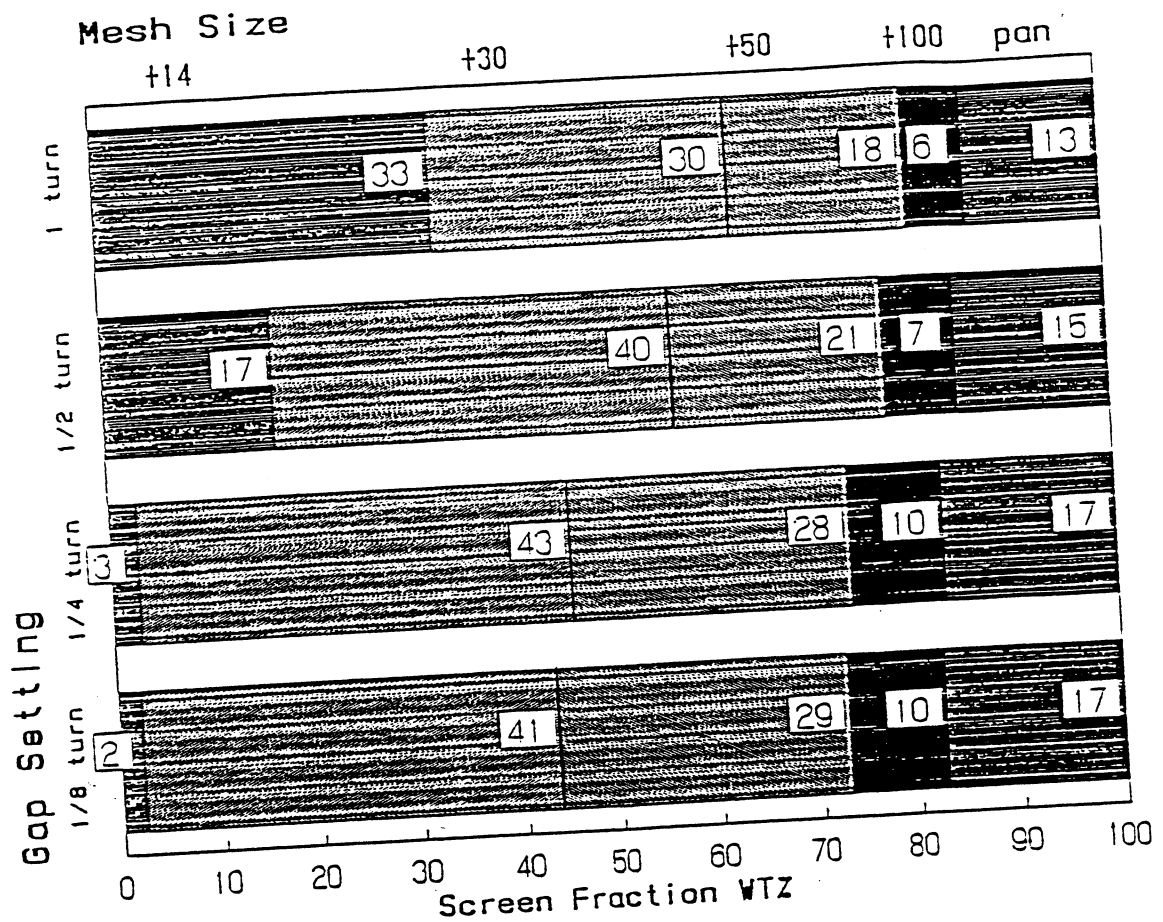
Waste shell specimens were roll crushed, at four different roll settings. The rolls were set and measured by turns of the roll-adjusting screw, which advances the roll approximately one inch per five turns. The gap set describing numbers (1, 1/2, 1/4 and 1/8) refer to adjusting screw turns, backing up from a closed (touching) roll position.

Five to seven kg. of shell was crushed per gap setting. The crushed material was riffle split to obtain 3 samples of 200 to 300 gms. each. These 3 samples from each gap setting were screen separated at the 14, 30, 50 100 mesh and pan (-100) levels to measure the particle size distribution for the material (see Figure 10).

These screens were chosen because 30, 50 and 100 meshes are common stucco product designation sizes. The 14 mesh, larger than common investment shell components, was included as a cut-off point, to ensure the extent of the comminution. The 100 mesh is also a low-end practicable particle size for efficient operation of the proposed mineral processing methods.

Sieve screen run repetitions were recombined and riffle split to obtain samples; larger particle size (+30, +50, +100) samples from the 1/4 turn roll set were mounted and sectioned for inspection with SEM images.

The smallest particles, the pan(-100) fraction, were ground to -325 mesh size for X-ray diffraction (XRD) phase analysis. This information is presented for the mid-range (1/2 turn) setting and the narrowest (1/8 turn) setting (see Figure 11).



- 1 Turn = 0.2"
 1/2 Turn = 0.1"
 1/4 Turn = 0.05"
 1/8 Turn = 0.025"

Figure 10. Sieve Screen Particle Size Analysis, Four Roll Settings.

Summary- Screen Analysis.

- Decreasing the roll gap settings;
- (1) Largely eliminated the oversize fraction (+14 mesh)
 - (2) Reduced oversized fractions to particle sizes appropriate for backup stucco (+30, +50).
 - (3) Did not greatly increase the undersize fractions (+100 and pan).

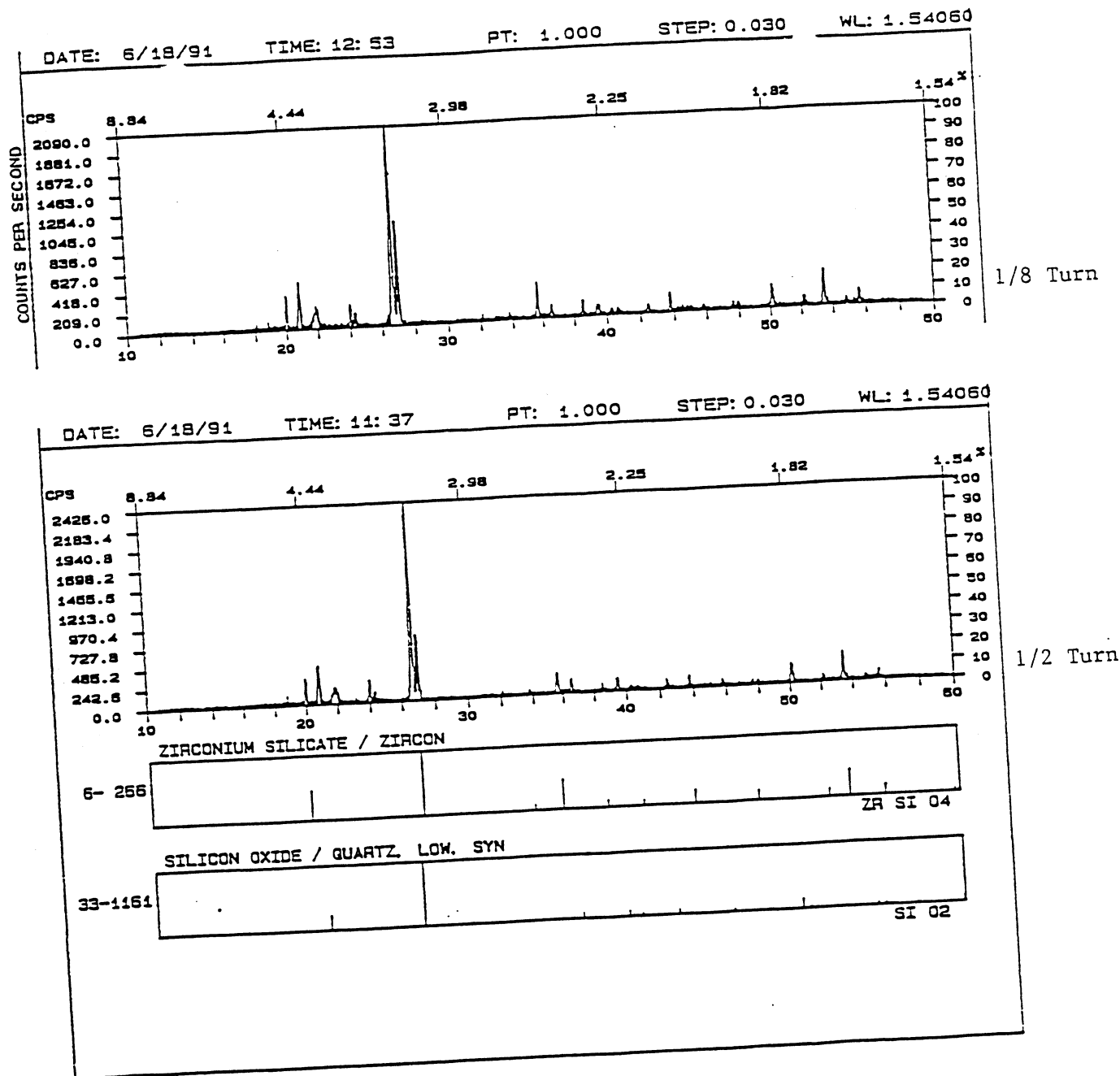


Figure 11. XRD Diffraction Patterns for 1/2 and 1/8 Roll Gaps.

Summary- XRD analysis

The pan fraction was predominantly silica, with minor zircon and no mullite. Zircon content increased slightly with narrower roll gap settings.

Summary- Microscopic Analysis of Shell Systems

Appendices I-IV represent the various microscopic methods utilized to identify and characterize typical investment casting shell materials. The four methods utilized were scanning electron microscopy, optical microscopy, cathodoluminescence, and reflected light microscopy. The specific features which each of these techniques accent are described in the figure captions for each of the micrographs.

The shell systems can be generally characterized into three parts:

1. Stucco from the backup zones, mainly clean, but some particles did have adherent silica films;
2. Agglomerations of the prime coat compositions, mixed zircon, silica and mullite; and
3. Prime stucco coat refractory agglomerations of silica and zircon.

The reflected light and cathodoluminescence microscopy appear to be the best techniques to clearly identify the laminated shells various constituents. These methods offer a qualitative approach to characterizing "groupings" of typical shell systems. They also can be used to compare the effectiveness of various reclamation and separation technologies.

CHAPTER TEN

CLASSIFICATION-

Classification techniques separate mineral mixtures on the basis of settling velocity of particles falling through a fluid medium, usually water. These techniques are commonly used for particles too fine for efficient screen sorting, but the same principles will apply to gravity concentration techniques.

Settling Particles-

In a viscous medium, a falling particle accelerates at a decreasing rate, quickly reaching a terminal velocity, then falls at this uniform rate. This velocity is determined by gravitational and fluid resistance force achieving an equilibrium.

A spherical particle, diameter- d_p and density- D_p , falling under gravity- g , through a viscous medium of density- D_f in free settling conditions is acted on by a downward gravity force- mg , an upward buoyant force due to displaced fluid- $m'g$, and a upward force from fluid drag resistance- Φ . The equation of motion is then [39]

$$m g - m'g - \Phi = m \delta x / \delta t \quad \text{Eqn. 7}$$

At the terminal velocity, $\delta x / \delta t$ is zero, then

$$\Phi = (m - m') g \quad \text{Eqn. 8}$$

Substituting for specific fluid and particle conditions,

$$\Phi = \pi/6 \cdot d^3 (D_s - D_f) g \quad \text{Eqn. 9}$$

Viscous And Turbulent Fluid Resistance-

Fluid resistance character depends partly on the velocity of descent. At low velocities, a layer of fluid travels with the particle and fluid a short distance away is motionless. The resistance is due to the shear between the fluid layers, and is termed viscous resistance. At higher velocities, the dominant resistance is due to fluid displacement by the advancing particle, and is known as turbulent resistance.

Stokes' Law For Settling Particles-

Stokes deduced an expression for entirely viscous resistance, with viscosity- n , and terminal velocity- v .

$$\Phi = 3 \cdot \pi \cdot d_p \cdot n \cdot v \quad \text{Eqn. 10}$$

Substituting in equation 9 and rearranging, the expression for the terminal velocity of a Stokes' particles, known as Stokes' law, is

$$v = \left[\frac{g \cdot d_p^2 \cdot (D_s - D_f)}{18 \cdot n} \right] \quad \text{Eqn. 11}$$

Newtons Law For Settling Particles-

Newton assumed drag force was entirely due to turbulent resistance, deducing Newton's Law

$$\Phi = 0.055 \pi \cdot d^2 \cdot v^2 \cdot D_f \quad \text{Eqn. 12}$$

substitution again in equation 9 gives

$$v = \left[\frac{3 \cdot g \cdot d_p \cdot (D_s - D_f)}{D_f} \right]^{\frac{1}{2}} \quad \text{Eqn. 13}$$

Stokes' And Newton's Laws Regimes-

Stokes law is valid for particle diameters below about $50\mu\text{M}$. Newton's law holds for particles larger than about 0.5 cm. Experimental data for the intermediate particle size range, which is the size range encountered in most fluid classification schemes (and in the current reclamation material) does not fit either law exactly but falls somewhere in between.

However, both laws indicate that the terminal velocity of a particle in a specific fluid is a function only of the particle size and density. The practical result of these factors are reinforced by observations-

If two particles are of the same density, the larger diameter particle has a higher terminal velocity.

If two particles are the same diameter, the denser particle has a higher terminal velocity.

Free Settling Ratio-

Consider particles of two different minerals, α and β , with respective values of density-D and diameters- d settling at the same terminal velocity. With Stokes' law

$$\frac{d_{\alpha}}{d_{\beta}} = \left[\frac{D_{\beta} - D_f}{D_{\alpha} - D_f} \right]^{\frac{1}{2}} \quad \text{Eqn. 14}$$

This is known as the Free Settling Ratio for Stokes' law, or the ratio of particle diameters required for two different density particles to settle at the same rate.

With Newton's Law, the corresponding Free Settling ratio is

$$\frac{d_{\alpha}}{d_{\beta}} = \left[\frac{D_{\beta} - D_f}{D_{\alpha} - D_f} \right] \quad \text{Eqn. 15}$$

The different exponents of the two expressions demonstrates why the effect of density differences on particle settling is more significant for classification of larger particle sizes.

Hindered Settling Ratio-

As the proportion of solids in a pulp increases, the interactions from particle crowding becomes significant and the terminal velocity decreases. The pulp of particles and fluid acts as a heavy liquid, whose density- D_p and viscosity is that of the pulp. This condition is known as hindered settling.

In the hindered settling condition, higher density and viscosity of the pulp increases the range of turbulent resistance regimes, so Newton's Law applies to a smaller size range of particles, and using the pulp density as the liquid density, the hindered settling ratio becomes

$$\frac{d_{\alpha}}{d_{\beta}} = \left[\frac{D_{\beta} - D_p}{D_{\alpha} - D_p} \right] \quad \text{Eqn. 15}$$

The consequence of hindered settling ratio is to reduce the effect of particle size, and increase the effect of density differences on classification. The Hindered Settling Ratio is always greater than the Free Settling Ratio, and the more concentrated the pulp, the greater the difference between particle diameters with equal settling rates.

To separate the components of investment shell comminution processes, hindered settling classifier devices would be very applicable. The various particle compositions, characterized by differing densities but overlapping particle sizes, could be separated with one of the many hindered settling type classifiers.

CHAPTER ELEVEN

CONCENTRATION PROCESSES-

The products of any liberation treatment must be separated into components, concentrating the useful materials for further use, removing the less valuable portions for disposal, and perhaps retaining a middling fraction to feed additional recovery treatments.

Mineral concentration methods exploit physical property differences existing among the minerals to be separated. The most common processes are based on specific gravity, surface chemistry, or either magnetic or electric susceptibility properties. [36] Specific gravity methods separate particles according to the differential movement of particles in hydraulic currents due to mass effects. Froth flotation involves manipulation of the surface chemistry, rendering mineral surfaces aerophilic or aerophobic, and introduces a stable froth of air bubbles which attach to and lift the aerophilic fractions. Magnetic susceptibility or high tension separators use magnetic susceptibility or conductivity differences to route particles through a separator.

Specific gravity methods, particularly heavy medium separation, are recommended as suitable for investment shell component reclamation. A discussion of gravity concentration is given after alternative methods are briefly criticized.

High Tension Separation-

The heavy mineral sands from which zircon is derived are partially processed with high tension separation. However, the primary separation required to retrieve aluminosilicates and zircon from investment shells must remove silica phases. Silica and zircon are similarly non-magnetic and -conducting, and are not separated by magnetic or high tension methods. [36] For mullite separation from other components there are no useful effects either.

Froth Flotation-

Froth flotation is a viable possibility which has been studied by Smith and Llewellyn and is discussed elsewhere in this report [34]. Flotation methods could be applied to separation of some fractions of investment casting shell materials, but only after extensive liberation of the highly interlocked zircon and silica components. Such liberation would require the expense of

a very fine grinding, probably to the original flour particle size, or a preliminary chemical removal of silica, at which point flotation seems redundant.

Because the zircon content is limited to a narrow zone in most shells, preconcentration of the zircon-rich fractions would be beneficial in reducing reagent consumption, operation costs and required equipment capacity for any subsequent recovery operations.

Gravity Separation-

There are a variety of gravity concentration methods with possible applications to investment shell component recovery. These methods require some density difference between the gangue and the values. The concentration criterion (CC) [37] indicates the feasibility of the separations possible, by comparing the specific gravities of the heavy mineral- D_h , the light mineral- D_l and of the suspending fluid- D_f ,

$$CC = \left[\frac{D_h - D_f}{D_l - D_f} \right] \quad \text{Eqn. 16}$$

If the absolute value of the concentration criteria, $|CC| \geq 2.5$, then gravity separation is relatively easy and effective. If the $|CC|$ is less than this value efficiency drops, until by a $|CC| \leq 1.25$, gravity methods are not commercially feasible.

High alumina (70%) aluminosilicate stucco, $D_h = 2.85$, requiring separation from fused silica of $D_l = 2.1$ would require a liquid of $D_f \geq 1.6$ to operate at the ideal CC of 2.5. The separation of crystalline silica of $D_l = 2.6$ from the same stucco at close particle sizes would require a liquid $D_f = 2.3$.

These values of pulp density are achievable with several different materials, discussed in the next section- Heavy Medium Separators.

CHAPTER TWELVE

HEAVY MEDIUM SEPARATORS-

Heavy medium separators (HMS) [34, 38-40], known also as sink-float separators, employ a liquid with a density whose value lies between the density of the minerals to be separated. Industrial operations use a water suspension pulp of a heavy mineral suspended in water, which behaves as a heavy liquid.

The most significant advantage of HMS is the ability to achieve sharp separations of materials, even between materials of very similar densities. The larger the particle size at which this difference occurs, the more efficient HMS will be. With particles of 3 mm. diameter, separation can be effective with specific density difference of 0.1 and less. [34] A major expense of the process is the additional equipment required to recover the media from the concentrate.

Heavy Medium Suspensions-

Below about a 30% volume concentration, finely ground particle suspensions in water act as Newtonian fluids; particles can move through the slurry in the direction any existing density difference dictates, with only viscous resistance. Above this concentration, the viscosity increases in a non-Newtonian manner, and some yield shear stress is required to set particles into motion. Small or near-pulp-density particles are locked in place, but motion imparted by paddles, air injection or even other settling particles can provide the necessary shearing force to begin motion.

To maintain stable suspensions of high density, the finely ground particles of high specific gravity are agitated. An ideal HMS slurry component must be hard and corrosion resistant to avoid degradation, easily removed from the separated minerals and high-enough specific gravity to provide high pulp densities.

Ferrosilicon(15%Si) is recommended for the separation of investment casting components, allowing high pulp densities at moderate viscosities (Figure 12). This composition compromises corrosion resistance and magnetic susceptibility. The magnetic feature will allow recovery from reclaimed material with simple apparatus. Ferrosilicon is not wetted by water, and requires surfactants to maintain acceptable suspensions. The

ferrosilicon(15%) compositions used for heavy medium separations have been reported available as a by-product of abrasive (brown) fused alumina production. [35]

Two possible HMS separation schematics are depicted (Figure 13). There are many more designs in operation.

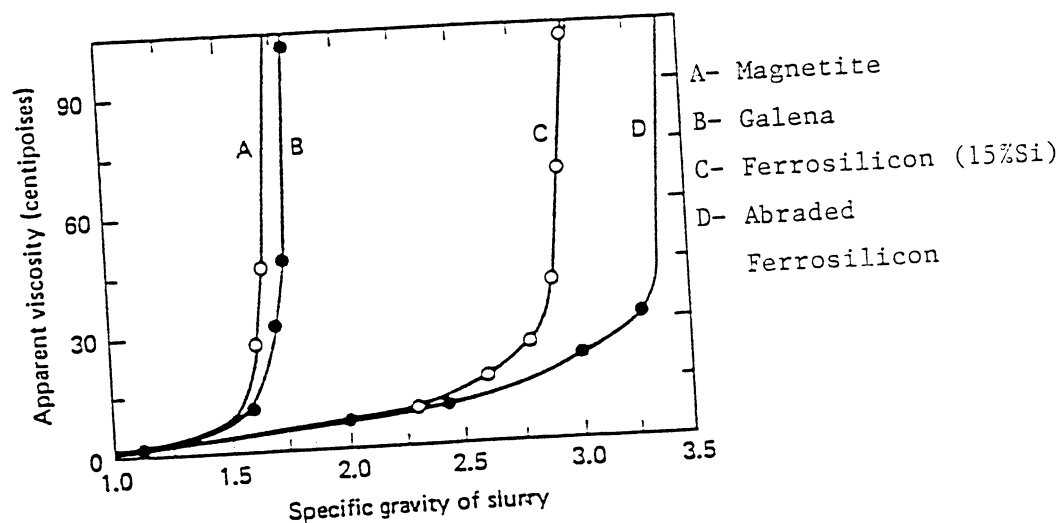


Figure 12. Apparent Viscosity Density Relationship for Heavy Medium Suspensions. [35]

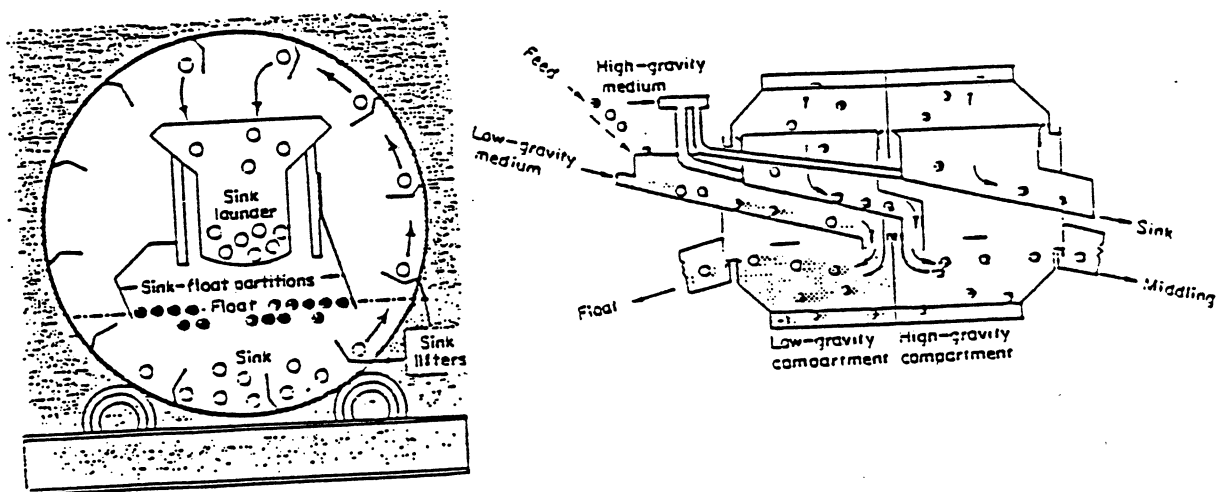


Figure 13. One and Two Compartment Heavy Medium Continuous Processing Drum Separators. [42]

CHAPTER THIRTEEN

RECLAMATION FACILITATING MODIFICATIONS-

There are some possibilities for modification to investment shells to facilitate reclamation without sacrifice of mold properties.

Thermal Processing

Thermal processing cycles to increase the crystallization of cristobalite from fused silica; although it is the presence of a highly flawed and disruptive cristobalite fraction which precludes 100% reuse of shell components, the extensive fracturing of this phase also occasions a high degree of valuable particle liberation, which can simplify the required processing. When crystalline silica fractures at the stucco surface and sloughs off the particle, reclaimed stucco is nearly indistinguishable from the virgin product. The small particle size of the fragmented silica compared to the grains of stucco and the other agglomerations also permits simple screening to raise the grade of the reclamation product at an early stage in the reclamation process.

Component Compositions-

The use of higher alumina content aluminosilicate stucco provides a more durable grain, better able to survive several reuse cycles. The higher density of this composition stucco will also increase the efficiency of specific gravity separations from crystalline silica.

Formulation of refractory mixtures should include consideration of the resulting composite density, avoiding compositions that would have similar values with other components. This will facilitate specific gravity separations.

Using pure refractory components, rather than mixtures, would reduce the separations that are required for a similar grade of concentrate. This may not be practical in the prime coats for reasons discussed in this report, but in the backup refractory use of fused silica with its subsequent crystallization would permit more efficient stucco liberation.

CHAPTER FOURTEEN

CONCLUSIONS AND RECOMMENDATIONS-

The investigation conducted revealed that typical investment shell systems contain relatively small quantities of zircon (2.5% - 5%). Additionally, the zircon is of high purity.

The additional components of the shell system are fused silica and/or aluminosilicates. The average foundry use 1.2 Million pounds of the materials annually. Additionally, the average cost/ton of this material, with disposal, is estimated at \$420/ton.

The results of the research indicate that effective reclamation of the components of the shell system is possible. However, the economics dictate that the cost/ton for reclaim should not exceed \$310.00.

It appears the most viable (economical) way to reclaim is for backup stucco material. This represents over 75% of the shell material and has the least amount of "purity" requirements.

The report also describes several useful methodologies to characterize individual shell system compositions. Of particular importance is the "Phase Distribution Graph" which is developed through SEM-XRD techniques. The semi-quantitative method describes the distribution of shell constituents from the mold-metal interface to the last layer. This methodology may prove useful to the investment casting industry as a quality control tool.

Additionally, reflect light and cathodoluminescence microscopy provides qualitative insight into the aggregate distribution of the shell system. These microscopy techniques also will assist the industry in characterizing and documenting their shell systems.

Early research results indicated that separation methods would not be sufficient to separate the shell into its original aggregate concentrations. Further work revealed that roll crushing should be utilized as the first step in the reclamation process. Crushing has been shown to be effective in producing satisfactory material to be used as a backup stucco.

Further screening and/or chemical separation methods are possible, but not seen as economical. Additionally, the final product which they would deliver would not be of a sufficient purity level to reuse in the primary slurry tanks.

It is recommended that equipment manufacturers, with a specific interest in reclaim, look into the feasibility of developing equipment to roll crush spent investment shells for backup stucco use. It appears that present economics may provide a return on investment for this system.

Finally, alternate sources of use for the spent shell materials should be investigated. Refractory suppliers, Rock Wool Manufacturers and sand foundries may have an interest in this waste material.

Rev.

REFERENCES CITED

- ✓1. R.A. Horton; "Investment Casting," *Metals Handbook--Casting*, 9th ed. vol 15, pp 253-269, ASM International, Metals Park, Ohio (1988).
- ✓2. Anon.; *Investment, Binders & Refractories for Precision Casting*, p 402, Ransom & Randolph, Maumee, Ohio.
- ✓3. J. Jackson; "Ceramics," *Investment Casting Institute Basics Course*, 4, ICI, Dallas, Texas.
- ✓4. F.E. Wagstaff; "Crystallization and Melting Kinetics of Cristobalite," *J. Am. Cer. Soc.*, 51 (8), pp 449-452 (1969).
- ✓5. Ainslie, Morelock, Turnbull; "Devitrification Kinetics of Fused Silica," *Symposium on Nucleation and Crystallization in Glasses and Melts*, ed Reser pp 97-107, The American Ceramic Society, Columbus, Ohio (1962).
- ✓6. T.E. Garner, Jr.; "Zircon," *Am. Cer. Soc. Bull*, 69 (5), pp 888-890 (1990).
- ✓7. W.T. Adams; "Zircon: From Curiosity to Commodity," *Am. Cer. Soc. Bull*, 68 (5), pp 1024-1027 (1989).
- ✓8. P.N. Charakraborty; "Characteristics of Zircon Sands and Their Application in Metal Casting."
- ✓9. P.N. Charakraborty; "Micromeritics of Zircon Sands," *Br. Foundryman* 66 (4) pp 93-101 (1973).
- ✓10. D.A. Templeton; "Zirconium" *Mineral Commodity Summaries 1991*, pp 186-187, U.S. Department of the Interior, Bureau of Mines, Washington, D.C. (1991).
- ✓11. W.T. Adams; "Zirconium and Hafnium," preprint from *Mineral Facts and Problems*, pp 1-15, U.S. Department of the Interior, Washington, D.C. (1985).
- ✓12. W.T. Adams; 1985 *ibid*.
- ✓13. G.W. Schiefelbein; Private correspondence (1990).
- ✓14. W.F. Wales; "Ceramic Binders and Aggregates for Precision Casting," *AFS Transactions*, 81, pp 249-259 (1973).
- ✓15. G.W. Schiefelbein; "Optimizing Performance of Colloidal Silica Binders in Investment Casting-Part 1," *Modern Casting*, 78 (9) pp 44-45 (1988).

REFERENCES CITED (continued)

- ✓16. L.M. Dahlin; "Colloidal Silica Systems for Investment Casting," *Precious Metals*, 27 (1) pp 81-83 (1969).
- ✓17. J. Jackson; "Ceramics," *Investment Casting Institute Basics Course*, 4, ICI, Dallas, Texas (1969).
- ✓18. I. Ohnaka; "Microsegregation and Macrosegregation," *Metals Handbook--Casting*, 9th ed. vol 15, pp 136-141, ASM International, Metals Park, Ohio (1988).
- ✓19. T.E. Garner, Jr.; "Mineralogy of Foundry Sands and Its Effects on Performance and Properties," *AFS International Cast Metals Journal* (1977).
- ✓21. R.L. Rusher; "Strength Factors of Ceramic Shell Molds," *AFS Cast Metals Research Journal*, 10 (4) pp 149-53 (1974).
- ✓23. M.J. Hendricks; "Ceramic Shell Permeability," paper presented at the 38th Annual Meeting of the ICI, Dallas, Texas (October 7-11, 1990).
- ✓25. G.W. Shiefelbein; 1988 *ibid*.
- ✓26. S.G. Ampian; "Clays," *Mineral Commodity Summaries 1991*, pp 40-41, U.S. Department of the Interior, Bureau of Mines, Washington, D.C. (1991).
- ✓27. R.L. Rusher; 1974 *ibid*.
- ✓33. Wright, Thomas, Wagner; "Howmet Reclaims 80% of Investment Casting Materials," *Foundry M&T*, (5) pp 60-61 (1984).
- ✓34. C.W. Smith, T.O. Llewellyn; "Recovery of Zircon from Investment Casting Molds," *Bureau of Mines Report of Investigations 8958*, U.S. Department of Interior, Washington, D.C. (1985).
- ✓35. P.A. Vesilind, A.E. Rimer; *Unit Operations in Resource Recovery, Engineering*, Prentice Hall, Inc., Englewood Cliffs, N.J. (1981).
- ✓36. R. Stevens; "Zirconia Engineering Ceramics," *Supplement to Intercceram*. 34 (2) pp 1-6 (1985).
- ✓37. Several Authors; "Zircon," *Annual Minerals Review, Bull of Amer. Cer. Soc.* (5) pp 64-68 (1985 to 1989).

REFERENCES CITED (continued)

- ✓ 38. B.A. Willis; *Mineral Processing Technology*, Pergamon Press, New York (1985).
- ✓ 39. B.A. Willis; *ibid*, p 145 (1985).
- ✓ 40. B.A. Willis; *ibid*, p 165 (1985).
- ✓ 41. B.A. Willis; *ibid*, p 164 (1985).
- ✓ 42. B.A. Willis; *ibid*, p 166 (1985).

OTHER REFERENCES USED

- ✓ M.F. Burditt; "Mold & Core Binders Keep Pace with Industry Demands," *Modern Casting*, 78 (6) (1988).
- ✓ S. Meng; "Study and Application of Water-Soluble Ceramic Cores for the Aluminum Alloy Casting," *Chinese Journal of Mechanical Engineering*, 25 (3), pp 94-97 (1989).
- ✓ P. Murza-Mucha; "A New Binder System for the Production of Aluminum Casting," *AFS International Cast Metals Journal*, (June 1981).
- ✓ Matusevich et al; "Basic Aluminum Nitrates as Binders for Silica-Free Molds," *Soviet Castings Technology*, (2) pp 24-27 (1989).
- ✓ D.F. Symonds; "Selection and Sizing of Heavy Media Equipment," *Des and Install of Conc. and Dewater Circuits*, Society of Mining Eng. of AIME, Littleton, Colorado (1986).
- ✓ D.N. Collins; "Principles of Dense Medium Cyclone Separation," *Mine and Quarry*, 17 (9) pp 41-46 (1988).
- ✓ T. Power; "Fused Minerals--The High Purity High Performance Oxides," *Industrial Minerals*, (July 1985).

Appendix I

SEM image analysis of characteristic stucco compositions.
Photographs identify the various constituents
of the shell material.

Appendix II

Optical micrographs of typical investment shells.

Appendix III

Reflected light micrographs of spent investment shells.

Appendix IV

Cathodoluminescence micrographs of spent investment shells.

^{these}
Use, Appendices (I-IV) taken
from Research Report
in AFS library

Per Dan T

11-24-92

K.

SEM 11305

characteristic stucco compositions.
the various constituents
material.

Photo # 21808

BSé image, + 14 fraction particles, carbon mounted.

Apparent particle categories;

white/gray- prime coat refractory agglomeration of fused silica and zircon.

gray, smooth- stucco grain, clean.

gray, textured- backup coat refractory agglomeration, fused silica.

gray, combined smooth/textured- stucco grain with adherent silica refractory.

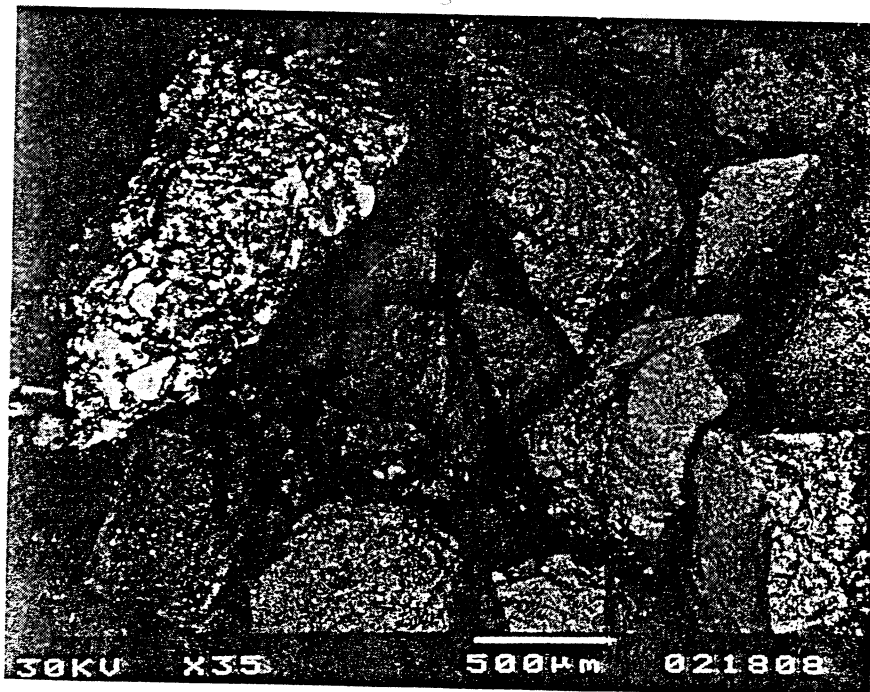


photo # 21811

BS_e image, +30 fraction particles. carbon mounted.

gray, smooth-	stucco grains of backup stucco size.
	some stucco with surface adherents evident
gray, textured-	mainly backup refractory agglomerations
gray/white-	fused silica/zircon agglomerations

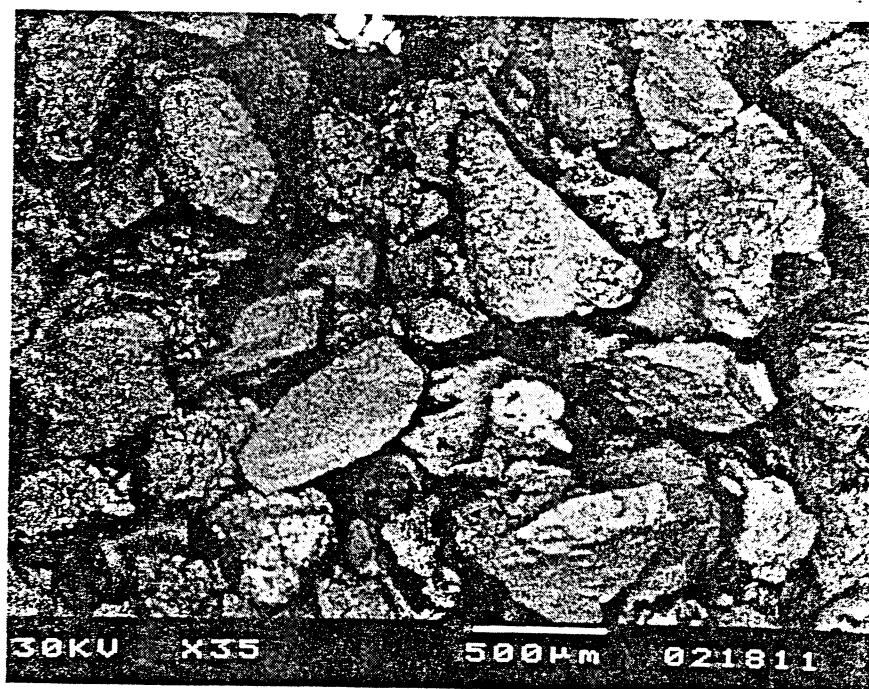


photo # 21802

BSé image. + 50 fraction particles. carbon mounted.

white/gray-	zircon/fused silica agglomerations. sand and flour sizes evident.
gray, smooth-	stucco, predominantly clean surfaced.
gray, textured-	silica agglomerations.

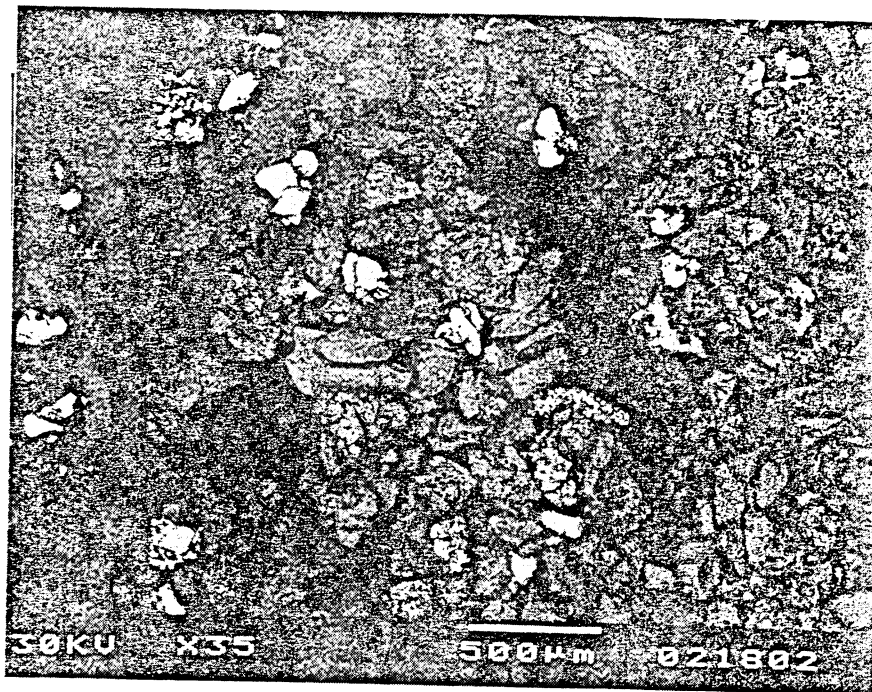


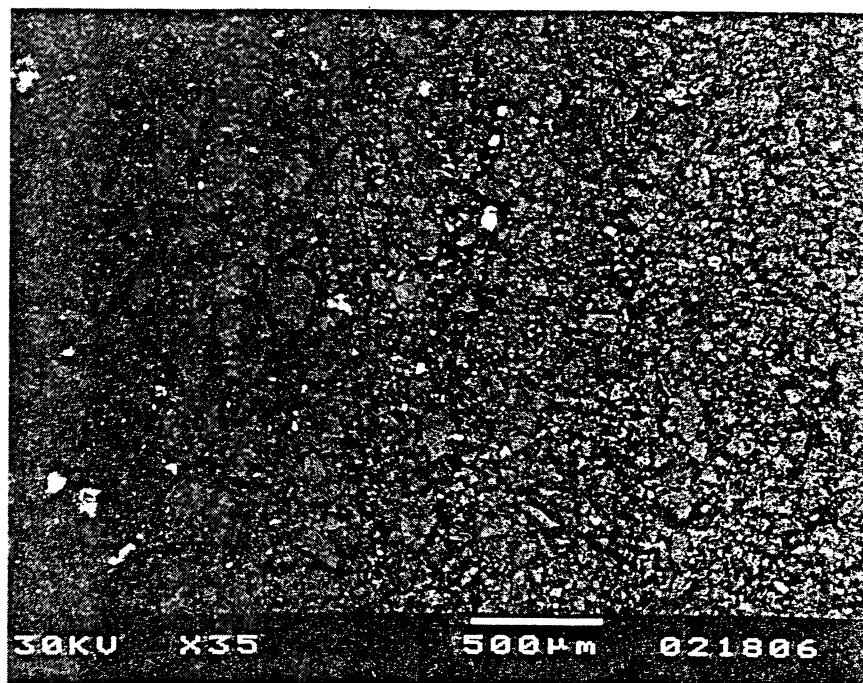
photo # 21806

BSE image. +100 fraction particles. carbon mounted.

gray, smooth- stucco, predominantly clean surfaced.

gray, small or textured- stucco and silica mixtures.

white- zircon particles, low concentration.

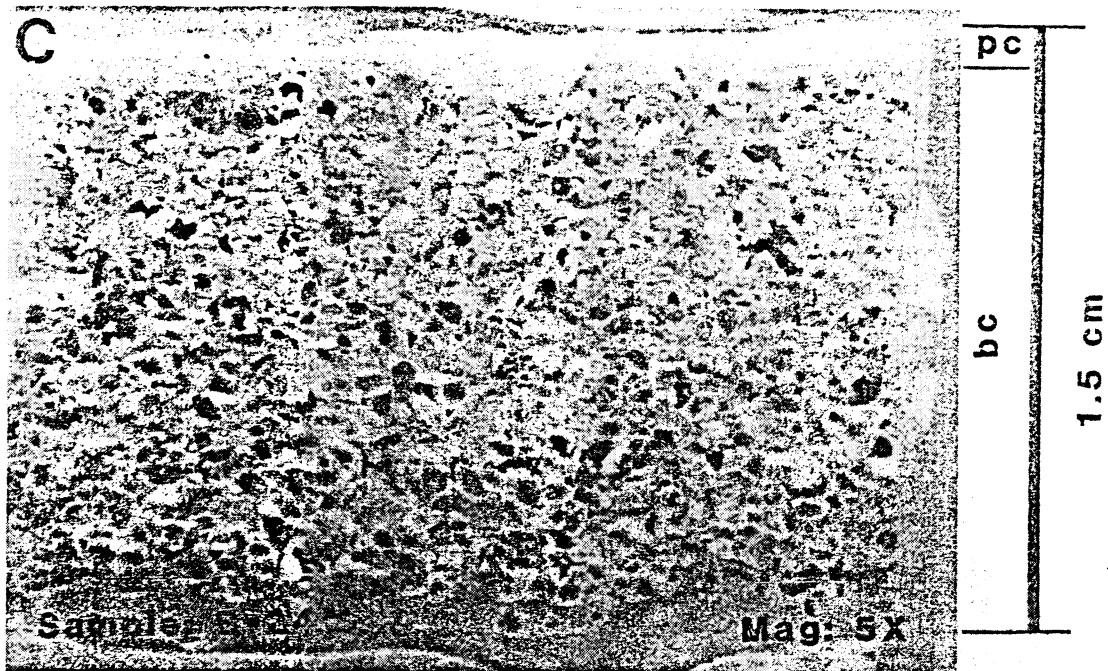


Appendix II

Optical micrographs of typical investment shells.



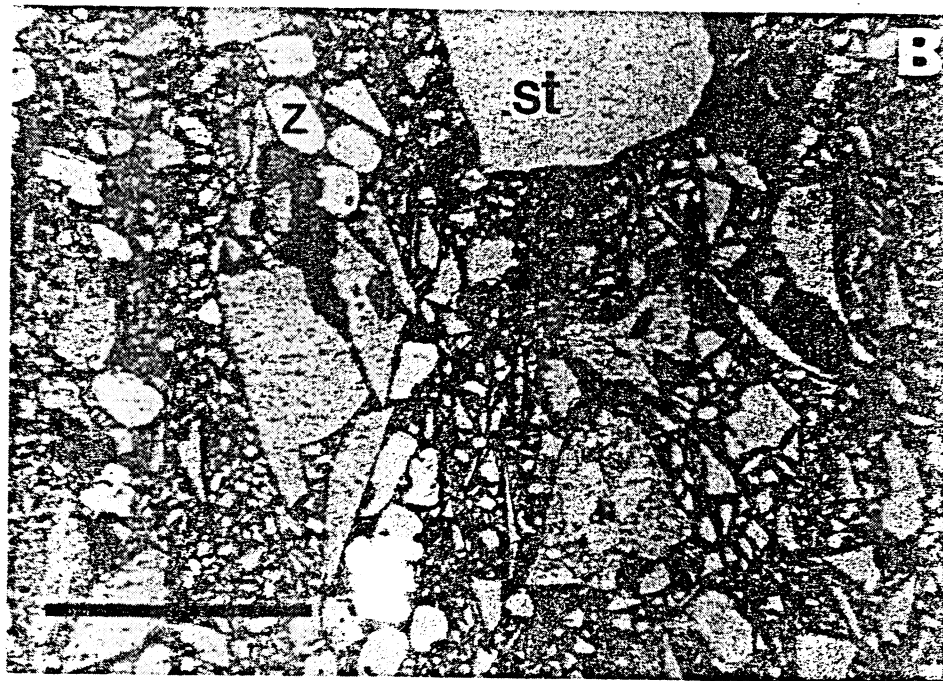
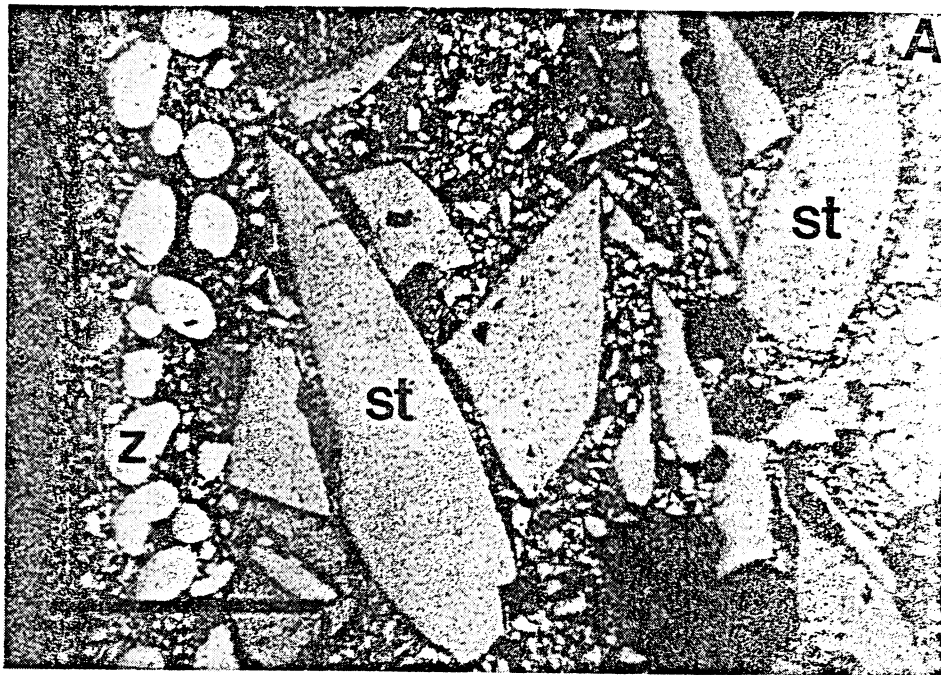
Low magnification showing composite layered structure of prime coat (pc) and backup coat (bc). Prime coat is a layer of zircon sand, crushed zircon fines, and refractory fines. Thickness of prime coat may change within the same shell. Backup coat is made up of large aluminosilicate aggregates (stuccos) and refractory fines combined with colloidal silica binder.



Low magnification showing composite layered structure of prime coat (pc) and backup coat (bc). Prime coat is a layer of zircon sand, crushed zircon fines, and refractory fines. Thickness of prime coat may change within the same shell. Backup coat is made up of large aluminosilicate aggregates (stuccos) and refractory fines combined with colloidal silica binder.

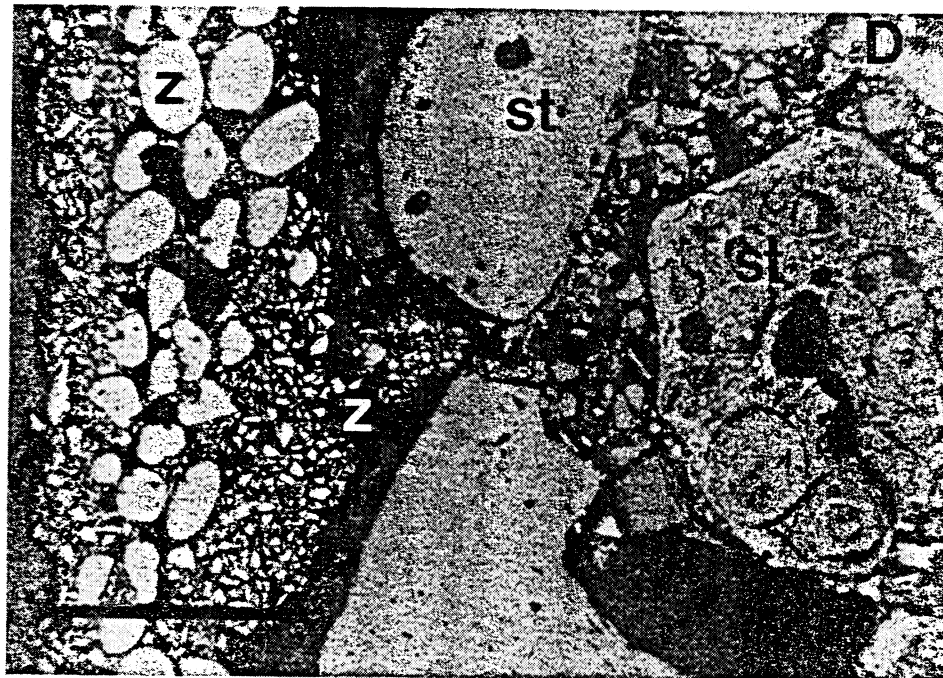
Appendix III

Reflected light micrographs of spent investment shells.



(A) Sample H, (B) sample M with double zircon sand layer. Magnification is 50X, and scale bar is 0.5 mm in all micrographs.

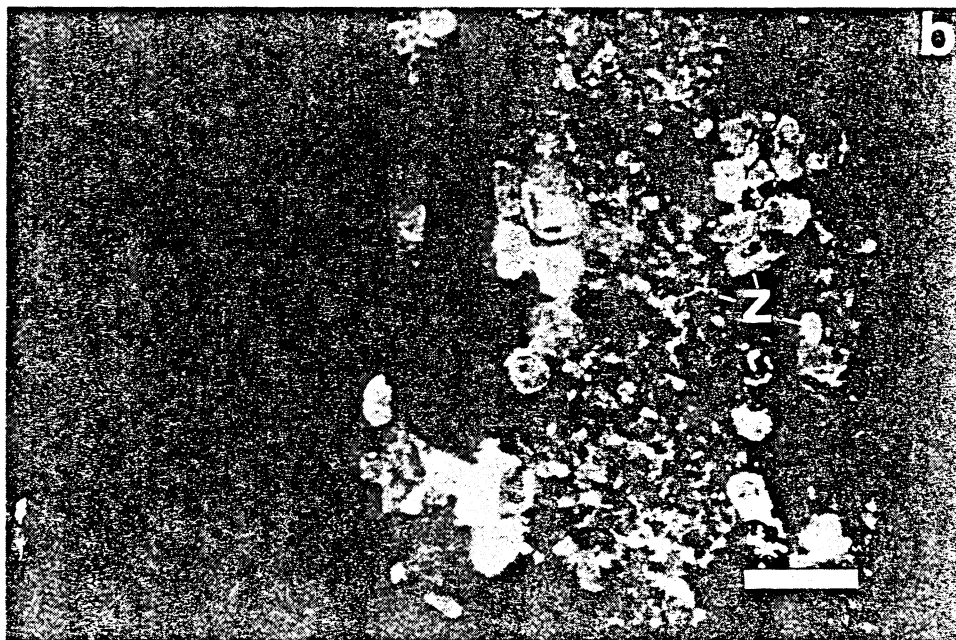
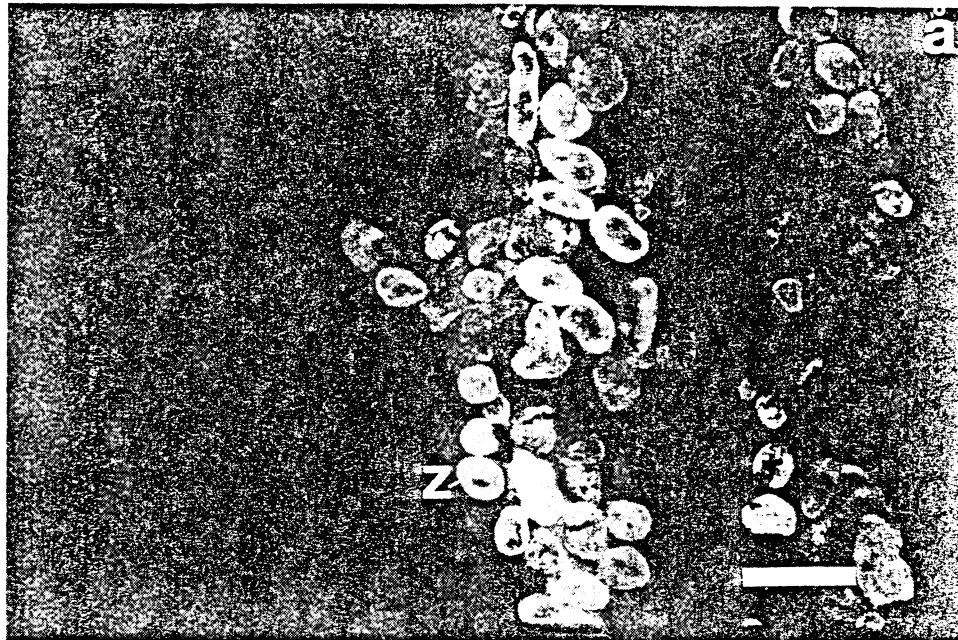
z: zircon, st: "stuccos", large aluminosilicate aggregates, fs: fused silica, and cri: cristobalite.



(C) Sample NP, a fused silica shell showing transformation of fused silica into cristobalite, and (D) Sample B showing a thick layer of zircon sands and fines in the prime coat.

Appendix IV

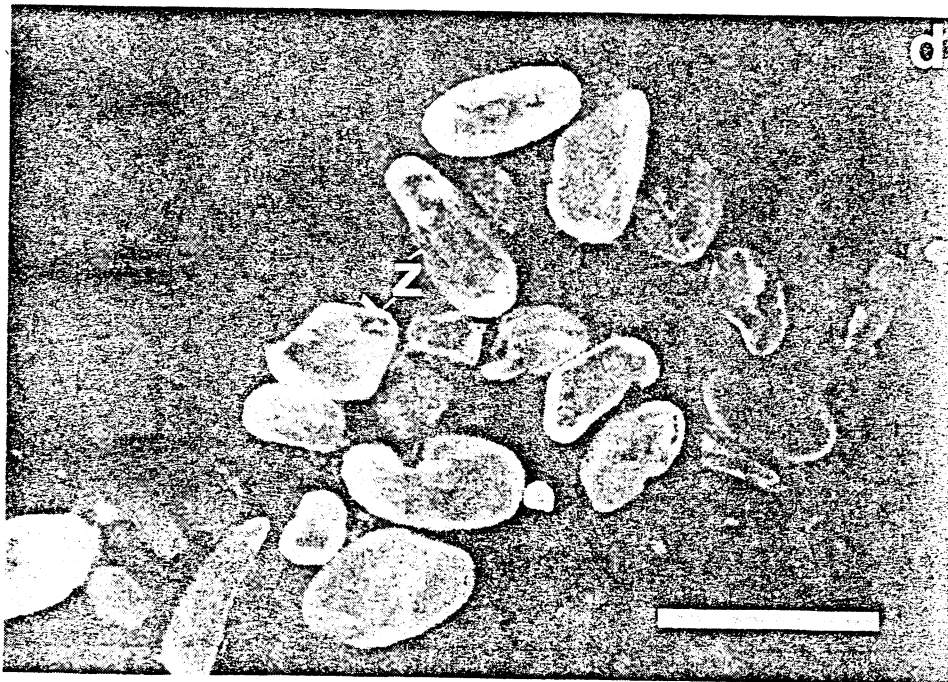
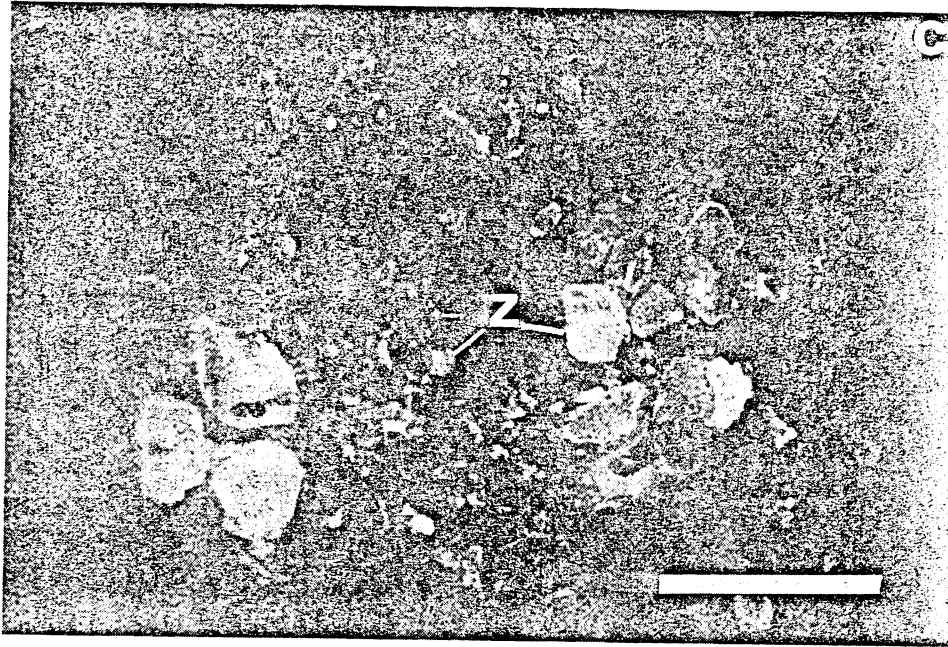
Cathodoluminescence micrographs of spent investment shells.



(a, b) CL of zircon sands and flour in the prime coat.

Magnification is 12.5X for a and b. Scale bar is 0.25 mm (250 micron) in all micrographs.

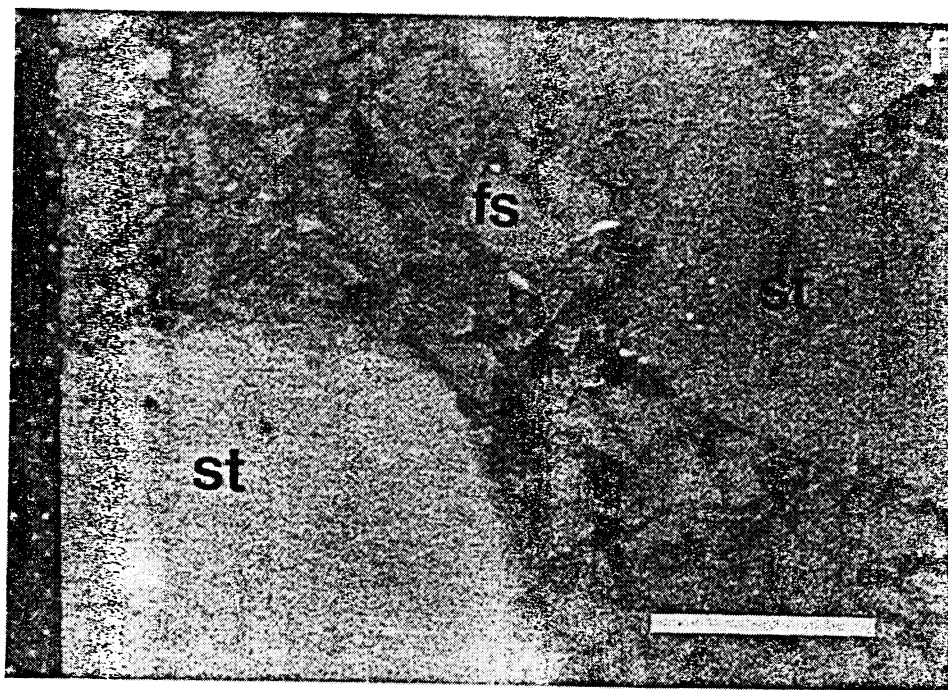
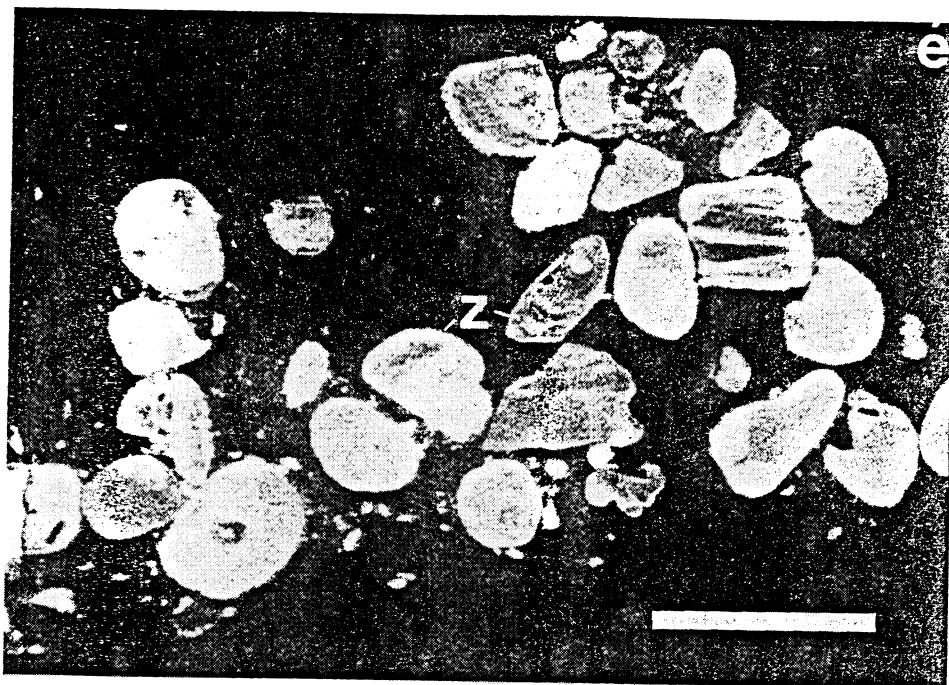
z: zircon, st: "stuccos", large aluminosilicate aggregates, fs: fused silica, and cri: cristobalite.



(c, d) CL or zircon sands and flour in the prime coat.

Magnification is 25X for c and d. Scale bar is 0.25 mm (250 micron) in all micrographs.

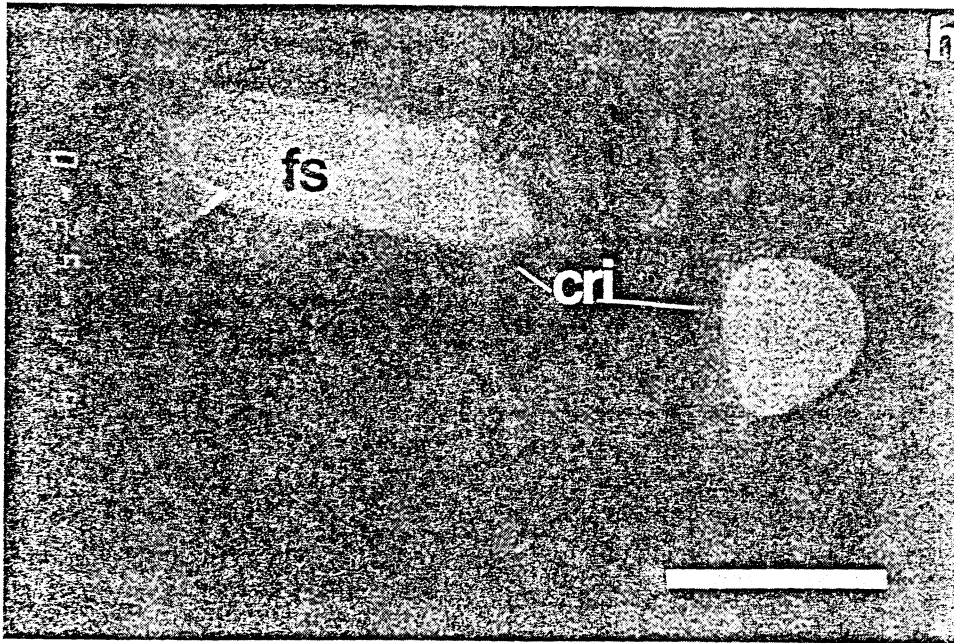
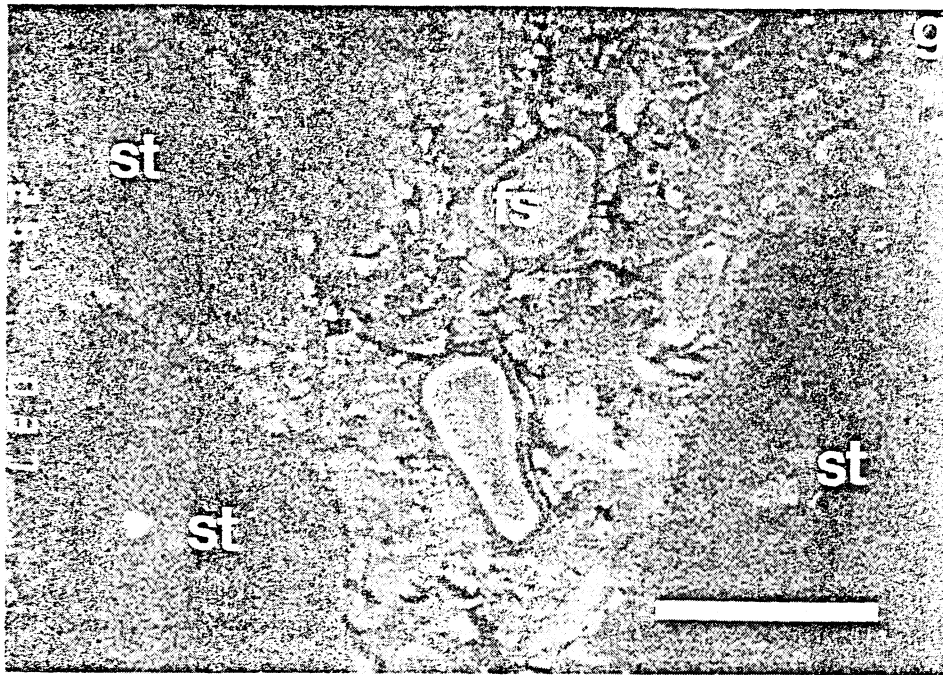
z: zircon, st: "stuccos", large aluminosilicate aggregates, fs: fused silica, and cri: cristobalite.



(e, f) CL microstructure of large aluminosilicate aggregates with varying composition and refractory fines (silica) in the backup coat.

10.52
Magnification is e and f. Scale bar is 0.25 mm (250 micron) in all micrographs.

z: zircon, st: "stuccos", large aluminosilicate aggregates, fs: fused silica, and cri: cristobalite.



(g) CL microstructure of large aluminosilicate aggregates with varying composition and refractory fines (silica) in the backup coat.

(h) CL of cristobalite around fused silica.

Magnification is 25X for g and h. Scale bar is 0.25 mm (250 micron) in all micrographs.

z: zircon, st: "stuccos", large aluminosilicate aggregates, fs: fused silica, and cri: cristobalite.

Glossary

- acid catalyst** An acidic substance which initiates a chemical reaction and enables it to proceed under milder conditions than otherwise possible.
- air bubbles** Entrapped air globules on a pattern during dip coating or investing that result in positive metal on the casting.
- air-cured mold** A mold which is cured in air without the application of heat or chemicals to accelerate the reaction.
- air-dried strength** Tenacity (compressive, shear, tensile, or transverse) of a refractory mixture after being air-dried at room temperature.
- air setting** The characteristic of some materials, such as refractory cements, core pastes, binders, and plastics, to take permanent set at normal air temperatures; as opposed to thermal setting.
- AQL** Acceptable Quality Level. A quality level established on a prearranged system of inspection using samples selected at random.
- as-cast condition** Casting without subsequent heat treatment.
- assembly** See *spruing*.
- autoclave** A vessel, usually of steel, which, under pressure and at elevated temperatures, removes wax from invested shells.
- autoclave accumulator** A vessel which stores steam from the autoclave.
- back draft** See *undercut*.
- back-up coat** The ceramic slurry of dip-coat which is applied in multiple layers following the first dip coat to provide a ceramic shell of the desired thickness and strength for use as a mold.
- binder** Liquid or solid additive to bond refractory particles.
- bleeder** A vent, open to air, which aids in the removal of wax from an investment shell.
- blister** A shallow blowhole with a thin film of the metal over it appearing on the surface of a casting.
- blowhole** Irregularly shaped cavities with smooth walls produced in a casting when gas, evolved during solidification of the metal, fails to escape and is held in pockets.
- buckle** Bulging of a large flat face of a casting, caused by dip coat peeling away from the pattern. It usually appears angular with some finning resulting from dip coat cracking.
- burn-out** Firing a mold at high temperature to remove pattern material residue.
- carburizing** A process that diffuses carbon into a solid ferrous alloy by heating the metal in contact with a carbonaceous material—solid, liquid or gas—to temperature above the transformation range and holding at that temperature. Carburizing is generally followed by quenching to produce a hardened case.
- caustic dip** Immersion in a solution of fused sodium hydroxide or equivalent, to clean the surface; or, when working with aluminum alloys, to reveal the macrostructure.
- charge** A given weight of metal introduced into the furnace.
- cluster** A group of expendable patterns on sprue and runners for casting purposes.
- cold shut** Lines on a casting surface resulting from incomplete fusion of metal streams appearing as flow lines on the casting.
- collapsible core** A metal insert made in two or more pieces to permit withdrawal from an undercut mold surface.
- colloid** A substance that is in a state of division preventing passage through a semipermeable membrane, consists of particles too small for resolution with an ordinary light microscope, and in suspension or solution fails to settle out and diffracts a beam of light. A system consisting of a colloid together with the gaseous, liquid, or solid medium in which it is dispersed.
- colloidal material** finely divided material less than 0.5 micron (0.00002 in.) in size, such as albumin, glue, starch, gelatin, and silica sol particles.
- cooling curve** A curve which shows the relation between time and temperature during the cooling of a metal sample. Since most phase changes involve evolution or absorption of heat, there may be abrupt changes in the slope of the curve.
- core** A metal insert in a die to produce a hole in a pattern. (See *preformed ceramic core*.)
- core cavity** The cavity produced in a casting by use of a core.
- core print** Projections attached to a pattern to form recesses in the mold at points where cores are to be supported.
- core shift** A variation from specified dimensions of a cored section due to a change in position of the core or misalignment of cores during assembly.
- core wires or rods** Reinforcing wires or rods for fragile cores, often preformed into special shapes.
- coupon** An extra piece of metal, either cast separately or attached to a casting, used to determine the mechanical or physical properties of the alloy.
- cristobalite** A polymorph of quartz. Silica occurring in white octahedra stable at high temperature.

- sodium hydroxide** A white, brittle, solid NaOH that is a strong caustic base which can be used to clean investment shell from casting.
- solidus** A line on a binary phase diagram representing the temperature at which freezing ends on cooling or melting begins on heating.
- solvent** The base metal or major constituent in a solution.
- spalling** The cracking and flaking of particles from the surface of castings or refractories; frequently due to thermal or mechanical shock. Mechanical spalling results from pressure stress.
- sprue** The portions of the mold cavity between pouring basin and runner cavity; applies to same portions of pattern setup and cast cluster. In top poured casting the sprue may also act as riser. Sometimes used as generic term to cover all gates, risers, and runners returned to the melting unit for remelting.
- sprue button** The pattern used to form the pouring basin.
- spruing** The act of attaching patterns to sprue. Also known as wax assembly.
- stress** The intensity (measured per unit area) of the internal distributed forces or components of force which resist deformation of a body. Stress is measured in force per unit area, for example pounds per square inch (p.s.i.).
- stress raisers** Factors, such as sharp changes in contour or surface defects, which concentrate stresses locally.
- stress relieving** A process of reducing residual stresses in a casting by heating the casting to a suitable temperature and holding for a sufficient time. This treatment may be applied to relieve stresses induced by casting, machining, welding, or other processing.
- stuccoing** The application of granular refractory to the wet dip coat on a heat disposable pattern or pattern cluster. See *investment shell*.
- suction pouring** Pouring metal into a mold while a vacuum is being drawn through the permeable mold base.
- tensile strength** The maximum load in tension which a material will withstand prior to fracture. In the case of ductile materials, fracture is preceded by elongation and consequent reduction in cross sectional area. The maximum stress is reached just prior to the necking down of the test piece. Tensile strength is calculated from the maximum load applied during the test divided by the original cross sectional area.
- test bar** Standard specimen bar designed to permit determination of mechanical properties of the metal from which it was poured.
- test coupon** See *coupon*.
- test lug** A lug cast as part of the casting and later removed for testing purposes.
- thermal conductivity** The property of matter by which heat energy is transmitted through particles in contact.
- thermal expansion** The increase in a linear dimension and volume of a material accompanying a change of temperature.
- thermal shock** The stress developed by rapid and uneven heating of a material.
- tie bar** A bar of metal connecting two comparatively thin sections of a casting separated by a narrow space. Its purpose is to prevent distortion of the sections. Often it is cut off the finished casting.
- undercut** A recess having an opening smaller than the internal configuration, thereby preventing mechanical removal of a one-piece core.
- vacuum casting** Pouring a mold under a vacuum.
- vacuuming** In investment casting the process of removing entrapped air bubbles from the investment or dip coat slurry before, during and/or after investing or coating by subjecting the mixture to a vacuum.
- vent** A small opening or passage in a mold or core to facilitate escape of gases when the mold is poured.
- warpage** See *distortion*.
- wax chill** See *prefill*.
- wax injection die** A precision metal die that has been cast over a master pattern or into which a cavity of the desired part configuration has been machined. Molten wax or plastic is injected into the cavity under pressure to form a precise wax pattern.
- yield point** The load per unit of original cross section at which a marked increase in deformation occurs without increase in load.
- yield ratio** The ratio of yield strength to ultimate tensile strength.
- yield strength** The stress at which a material exhibits a specified limit of permanent strain.
- Zahn cup** An apparatus used to measure the viscosity of a slurry.

Glossary

- acid catalyst** An acidic substance which initiates a chemical reaction and enables it to proceed under milder conditions than otherwise possible.
- air bubbles** Entrapped air globules on a pattern during dip coating or investing that result in positive metal on the casting.
- air-cured mold** A mold which is cured in air without the application of heat or chemicals to accelerate the reaction.
- air-dried strength** Tenacity (compressive, shear, tensile, or transverse) of a refractory mixture after being air-dried at room temperature.
- air setting** The characteristic of some materials, such as refractory cements, core pastes, binders, and plastics, to take permanent set at normal air temperatures; as opposed to thermal setting.
- AQL** Acceptable Quality Level. A quality level established on a prearranged system of inspection using samples selected at random.
- as-cast condition** Casting without subsequent heat treatment.
- assembly** See *spruing*.
- autoclave** A vessel, usually of steel, which, under pressure and at elevated temperatures, removes wax from invested shells.
- autoclave accumulator** A vessel which stores steam from the autoclave.
- back draft** See *undercut*.
- back-up coat** The ceramic slurry of dip-coat which is applied in multiple layers following the first dip coat to provide a ceramic shell of the desired thickness and strength for use as a mold.
- binder** Liquid or solid additive to bond refractory particles.
- bleeder** A vent, open to air, which aids in the removal of wax from an investment shell.
- blister** A shallow blowhole with a thin film of the metal over it appearing on the surface of a casting.
- blowhole** Irregularly shaped cavities with smooth walls produced in a casting when gas, evolved during solidification of the metal, fails to escape and is held in pockets.
- buckle** Bulging of a large flat face of a casting, caused by dip coat peeling away from the pattern. It usually appears angular with some finning resulting from dip coat cracking.
- burn-out** Firing a mold at high temperature to remove pattern material residue.
- carburizing** A process that diffuses carbon into a solid ferrous alloy by heating the metal in contact with a carbonaceous material—solid, liquid or gas—to temperature above the transformation range and holding at that temperature. Carburizing is generally followed by quenching to produce a hardened case.
- caustic dip** Immersion in a solution of fused sodium hydroxide or equivalent, to clean the surface; or, when working with aluminum alloys, to reveal the macrostructure.
- charge** A given weight of metal introduced into the furnace.
- cluster** A group of expendable patterns on sprue and runners for casting purposes.
- cold shut** Lines on a casting surface resulting from incomplete fusion of metal streams appearing as flow lines on the casting.
- collapsible core** A metal insert made in two or more pieces to permit withdrawal from an undercut mold surface.
- colloid** A substance that is in a state of division preventing passage through a semipermeable membrane, consists of particles too small for resolution with an ordinary light microscope, and in suspension or solution fails to settle out and diffracts a beam of light. A system consisting of a colloid together with the gaseous, liquid, or solid medium in which it is dispersed.
- colloidal material** finely divided material less than 0.5 micron (0.00002 in.) in size, such as albumin, glue, starch, gelatin, and silica sol particles.
- cooling curve** A curve which shows the relation between time and temperature during the cooling of a metal sample. Since most phase changes involve evolution or absorption of heat, there may be abrupt changes in the slope of the curve.
- core** A metal insert in a die to produce a hole in a pattern. (See *preformed ceramic core*.)
- core cavity** The cavity produced in a casting by use of a core.
- core print** Projections attached to a pattern to form recesses in the mold at points where cores are to be supported.
- core shift** A variation from specified dimensions of a cored section due to a change in position of the core or misalignment of cores during assembly.
- core wires or rods** Reinforcing wires or rods for fragile cores, often preformed into special shapes.
- coupon** An extra piece of metal, either cast separately or attached to a casting, used to determine the mechanical or physical properties of the alloy.
- crystalobalite** A polymorph of quartz. Silica occurring in white octahedra stable at high temperature.

crush An indentation, usually on the concave face of a casting, resulting from expansion of dip coat into the shell cavity after burnout.

cure To harden.

cut off Removing casting from sprue by refractory wheel or saw, arc-air torch or gas torch.

decarburization Loss of carbon from the surface of a ferrous casting as a result of solidification or heating in a medium, usually oxygen that reacts with the carbon. Lost carbon can be restored by heat treatment in an appropriate atmosphere.

degasification Usually a chemical reaction resulting from a compound added to molten metal to remove gases from the metal. Often inert gases are used in this operation.

degasifier A material employed for removing gases from molten metals and alloys.

delamination Separation into constituent layers.

dendrite A crystal that has a tree-like branching pattern; most evident in cast metals slowly cooled through the solidification range.

deoxidation Removal of excess oxygen from the molten metal; usually accomplished by adding materials with a high affinity for oxygen.

deoxidizer A material used to remove oxygen or oxides from molten metals and alloys.

descaling A chemical or mechanical process for removing scale or investment material from castings.

dewaxing The process of removing the expendable wax pattern from an investment mold or shell mold; usually accomplished by melting out with application of heat or dissolving the wax with an appropriate solvent.

die The metal form in which the cavity for producing heat-disposable patterns is cut or pressed.

die cavity The impression in a die into which pattern material is forced.

dip coat 1) In the solid mold technique of investment casting, an extremely fine ceramic coating called precoat, applied as a slurry directly to the surface of the pattern to reproduce maximum surface smoothness. The coated setup is surrounded by coarser, cheaper and more permeable investment to form the mold. 2) In the shell mold technique of investment casting, an extremely fine ceramic coating called the first coat, applied as a slurry directly to the surface of the pattern to reproduce maximum surface smoothness. The first coat is followed by other dip coats of different viscosities and usually contains different grading of ceramic particles. After each dip, coarser stucco material is applied to the still wet coating. A buildup of several coats forms an investment shell mold.

discontinuity An opening in a part representing an actual break in continuity; it connotes flaws rather than intended openings.

distortion Deformation (other than contraction) that develops in a casting between solidification and room temperature; also deformation occurring during heat treating and high temperature service.

double firing The act of heating the ceramic shell twice for a given time at temperature.

dowel A pin of various types used in the parting surface of parted patterns or dies to assure correct registry.

ejector pins Movable pins in pattern dies which help remove patterns from the die.

elongation Amount of permanent extension in the vicinity of the fractures in the tensile test; usually expressed as a percentage of original gauge length, such as 25% in 1 inch.

endurance limit A limiting stress, below which the metal will withstand, without rupture, an indefinitely large number of cycles of stress.

endurance ratio The ratio of endurance limit to ultimate strength. For most ferrous metals, this value lies between 0.4 and 0.6. Endurance ratio equals endurance limit divided by ultimate strength.

etching In metallography, the process of revealing structural details by preferential attack of reagents on a metal surface. Employed in production of some investment castings to reveal surface grain condition.

ethyl silicate A strong bonding agent for sand and refractories which deposits silica upon drying from a water solution. Used in preparing molds in the investment casting process. Also known as tetraethyl silicate or TES.

expendable pattern material See *heat disposable pattern*.

fatigue tendency for a metal to break under conditions of repeated cyclic stressing considerably below the ultimate tensile strength.

fatigue crack or failure A fracture starting from a nucleus where there is an abnormal concentration of cyclic stress and propagating through the metal. The fracture surface is smooth and frequently shows concentric (sea shell) markings with a nucleus as a center.

fatigue strength Maximum stress that a metal will withstand without failure for a specified large number of cycles of stress. Often confused with endurance limit, to which it is related.

feeder, feeder head A reservoir of molten metal to compensate for the contraction of metal as it solidifies, thus preventing voids in the casting.

filled wax Pattern wax which contains a given percentage of filler.