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REFINING PRACTICES AT SIMCOA OPERATIONS PTY LTD

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ABSTRACT

In Simcoa's drive to completely satisfy our customer requirements, in both the Chemical and Metallurgical industries, Simcoa identified the need to be able to adjust the ladle chemistry when necessary to ensure the wide range of silicon grades required by our global customer base can be readily and consistently produced.

This study continues the work which was commenced in late 1993[1] to ascertain the impact of varying the refining conditions or ladle additions on the chemistry and microstructure of the cast silicon product.

INTRODUCTION

One of Simcoa's key advantages is having control over the production and supply of its main raw materials, namely charcoal and quartzite. By blending different grades of quartzite, varying the ratio of low ash coal to charcoal and the addition of limestone to the furnace, the tapped silicon chemistry can be controlled over a wide range in order to produce the required grades.

Under certain operating conditions, there is a requirement to be able to adjust the silicon chemistry still further in order to meet the needs of Simcoa's broad customer base. This entails flux additions to the ladle in order to reduce the aluminium and calcium to very low levels and metal or alloy additions to increase the iron, aluminium or calcium levels to meet specific customer requirements. This study continues to address the concerns arising from ladle additions[1].

In a continuing search to delight our customers in both the Chemical and Metallurgical Industries, Simcoa identified a need to be able to adjust the minor

element chemistry in the ladle. Adoption of this strategy allows the wide range of silicon grades needed by Simcoa's global customer base to be readily and consistently produced.

PROCESS AND PRODUCT CAPABILITY

As previously reported [1], a number of different aspects of the furnace operation at Simcoa are under study to determine the impact that both raw materials and the process have on the variability of the tapped silicon chemistry. Table 1 lists the major causes which have an effect on the C*pk* of the tapped metal, which are ranked in order of increasing importance.

It is believed that once the variation of tapped metal chemistry, weights, temperature, recovery and slag losses are controlled within close limits, then the control over the refining and casting operations will be more successful and hence the variation within a particular grade will be significantly reduced.

Table 1 Major causes which effect the C*pk* of tapped silicon

Ranking	Cause
1	Coal - Sizing
2	Quartz - Contamination
3	Charcoal Reactivity
4	Furnace Rotation
5	Use of Correction Mixes
6	Charcoal - Variation in Carbon Analysis(Sampling)
7	Coal - Ash Content Variation
8	Training and Experience Of Operators
9	Charcoal Sizing
10	Operating Resistance (electrode penetration)
11	Furnace Cfix Changes
12	Furnace Mix Segregation
13	Communications - Management and Shift Crews
14	Raw Material Loading Procedures
15	Shift Crew Inter-Communication
16	Charcoal Fines - Generated in Handling
17	Plant Availability
18	Charcoal - Variation in Carbon Analysis(Retort Operation)
19	Limestone - Addition Procedures
20	Tapping Practices
21	Cfix Changes - Proc. for Correcting for Changes in Charcoal
22	Stoking / Feeding Practices
23	Quartz - Variation in Analysis from Mine
24	Operating Procedures
25	Optimum Furnace CFix Operating Level

The process capability index (C*pk*) was selected to chart the improvements achieved since the inception of the project. This index measures how 'capable' the process is at producing a particular grade or product. As the *Cpk* is calculated from both the production statistics and the grade specification it becomes a measure of how "skewed" the product is in relation to customer's specification and the variability of the silicon produced during that particular customer's production run.

Initially the process capability of the four main grades was established to ensure that any changes or improvements could be benchmarked against the initial values. After extensive trials a comprehensive program for improving the process capability for the minor elements Fe, Al and Ca in the four main silicon grades produced at Simcoa was implemented.

The methods used to measure the C*pk* and its implications for both the process and production of silicon products at Simcoa have been detailed previously [1]. A brief description only is given here. Figure 1 displays the histogram for iron from Dec '93 to Jan '94. The distribution is non-normal and the variation in iron from tap to tap has resulted in a low C*pk* of 0.3 .

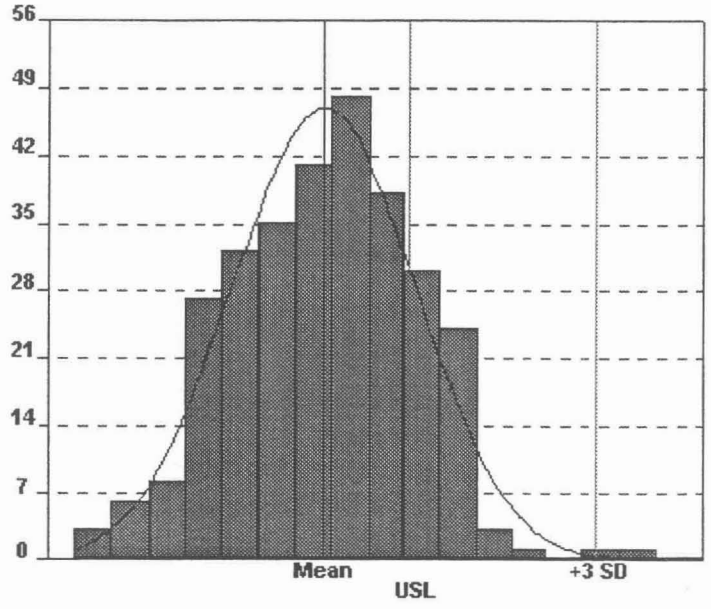

Figure 1: The histogram for iron, mean of 0.22 and C*pk* of 0.3 for the production period Dec '93 to Jan 1994

Figure 2, is the distribution for iron during the production period April to May '94, where the C*pk* has increased from 0.3 to 0.5. Although there has been some improvement for the iron capability, further improvements are still required to raise the C*pk* above the minimum value of 1. The ultimate goal of this work is to achieve a C*pk* of at least 2 for all the specified elements in Simcoa's silicon.

Control charts are used to establish that the process is in control and the analyses of all taps produced is used for calculating the C*pk*, for each grade during its production run.

Apart from the variation in the liquid silicon chemistry on a tap to tap basis, there is also significant variation in the cast silicon owing to segregation of the elements during cooling and solidification. The size and depth of the silicon castings and the rate of cooling have a significant effect on the degree of segregation within a cast. Hence during the crushing of metal from a single tap there will be a difference in the analysis of individual pieces of silicon.

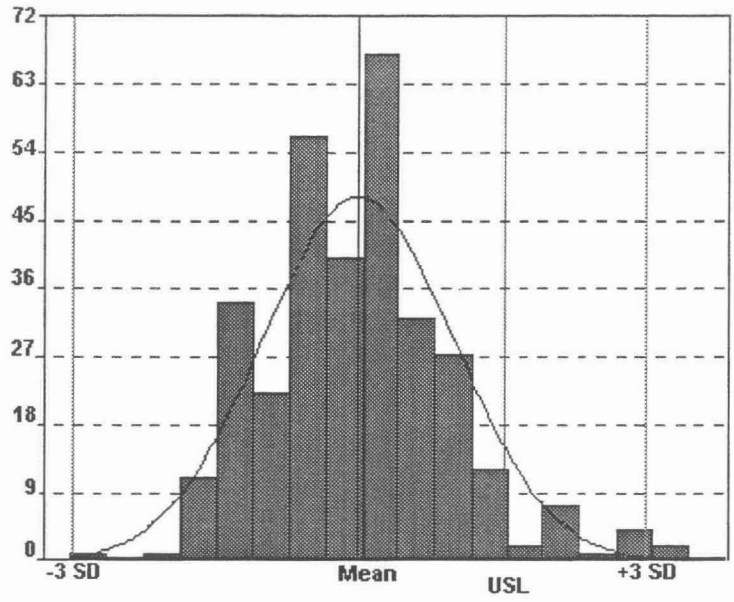

Figure 2: The histogram for iron, mean of 0.23 and C*pk* of 0.5 for the production period April to May 1994

As a part of Simcoa's drive towards ***total customer satisfaction or delighting the customer***, a program was initiated between Simcoa, the Chemistry Centre(WA) and Curtin University of Technology to gain a greater understanding of the process from the point at which silicon leaves the taphole to the stage where it is finally cast and cooled. Such an improved understanding should include taphole chemistry, refining, ladle additions and casting processes.

This program was driven by the need to understand the effects that alloy and flux additions have on the silicon chemistry and intermetallic morphology and composition, a factor which is important for the chemical industry. Also Simcoa supplies silicon in packaged sizes from 10kg to 21 tonnes to the metallurgical industry and hence it is important to assure our customers that the silicon grade is consistent in all the packaged forms.

TAPPING, REFINING AND CASTING OPERATIONS

Significant process improvements have been achieved in the tapping, refining and casting areas of the silicon production operation at Kemerton. A detailed description has been given previously[1,2].

Simcoa developed and installed its own ladle plug system for refining silicon. Silicon is tapped directly into covered 4 tonne ladles fitted with bottom refining plugs, through which metered air and oxygen are continuously injected to adjust the calcium and aluminium contents to the desired levels. The oxygen and air flow rates are adjusted to maintain temperatures at 1500°C and to achieve the desired silicon

grade. Off-grade silicon metal is added to the ladles as a coolant to control the temperature.

Owing to the low impurity levels of Simcoa's raw materials, a small quantity of limestone is added to the furnaces to increase the tapped calcium levels to between 0.2 and 0.3%. This is beneficial for both the furnace process[3] and refining operation where calcium combines with aluminium and silicon to produce a dense viscous slag which settles to the bottom of the ladle during refining. This is especially important for the production of chemical silicon grades, where oxide inclusions in the silicon have a detrimental effect on the performance of the reactors in the Methylchlorosilane (MCS) process[4,5].

Molten silicon metal is cast from the ladle into iron frames set on massive cast iron tables. A small quantity of crushed silicon is used as a pouring pad which protects the tables.

LADLE ADDITIONS

A detailed test program was undertaken at Simcoa to investigate the impact of ladle additions made during refining had on the minor element chemistry, and the silicon structure in the cast product.

The program involved the addition at specific times during the refining and tapping cycle of weighed quantities of either aluminium, limestone, iron or calcium disilicide. Some tests involved the adding to the ladle of a single species, while other tests used a combination of two to three species added to the ladle.

Liquid silicon samples were taken during the casting of each mould to determine the bulk silicon chemistry and to ascertain whether there was any significant difference in the Fe, Al, Ca or Ti levels from mould to mould, which would indicate whether there was any segregation of the above minor elements in the ladle.

The cast dimensions were 1200x1200x150mm and several casts from each tap were sampled at specific locations within the casts as follows:

- horizontally from the front of the cast near the target area (position A) to middle of the cast (B) across to the back of cast (C).
- vertically through the thickness of the cast on the above grid, from the top (T), middle (M) and bottom (B).

The sample locations are shown schematically in Figure 3.

Chemical, optical and electron microscopy techniques were used to identify differences, anomalies or specific phases which existed in both casts subject to additions and in those where no additions had been made.

The details of the additions and the tap and cast analyses are given in Table 2. All cast analyses were based on liquid samples taken during casting, except for the two

where iron was added to the ladle, which were averaged from the analysis of the samples taken from the chills.

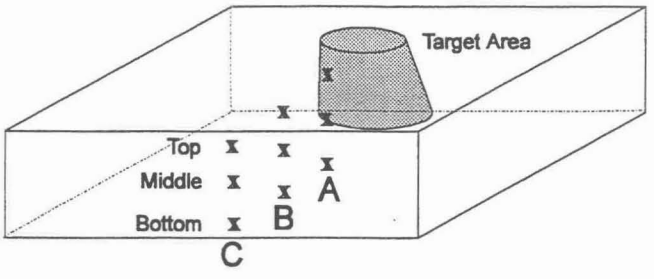

Fig 3. Schematic section of sample locations within the cast.

Table 2 Study conditions and results.

Code		Analysis %				Additions (kg)			
		Fe	Al	Ca	Ti	L'stone	$CaSi_2$	Al	Fe
T5M3	Tap	0.14	0.32	0.130	0.030				3.5
	Cast	0.23	0.14	0.003	0.030				
T6M4	Tap	0.25	0.43	0.190	0.040	40		3	
	Cast	0.25	0.27	0.036	0.036				
T6M1	Tap	0.14	0.35	0.180	0.030	40			3.5
	Cast	0.33	0.14	0.006	0.032				
T3M3	Tap	0.15	0.43	0.290	0.030				
	Cast	0.16	0.16	0.011	0.032				
T4M1	Tap	0.17	0.32	0.240	0.030	26	8	5	
	Cast	0.19	0.28	0.079	0.039				
T5M1	Tap	0.18	0.43	0.250	0.040	26			
	Cast	0.18	0.18	0.022	0.034				

RESULTS AND OBSERVATIONS

Results and observations from the study are listed below :-

1. Minor elements were concentrated in the middle section of the mould for casts without additions, while element concentration occurs in the middle and bottom sections of casts subject to minor element additions. This aspect is highlighted in Figures 4 and 5.

2. Minor elements were concentrated in the centre of the cast (position B in horizontal profile) which is indicative of the zone of final freezing. This is highlighted in Figure 6, where the positions A, B and C are sample locations which were equi-distant apart across the mould. The analysis at each point was the average of the top, middle and bottom samples from the cast.

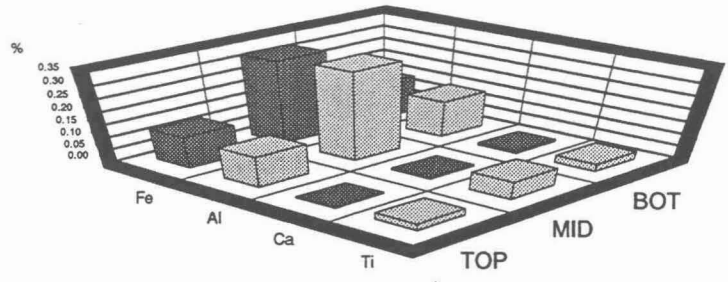

Fig 4. Minor element distribution in the vertical section of the cast, no ladle additions, sample - T3M3

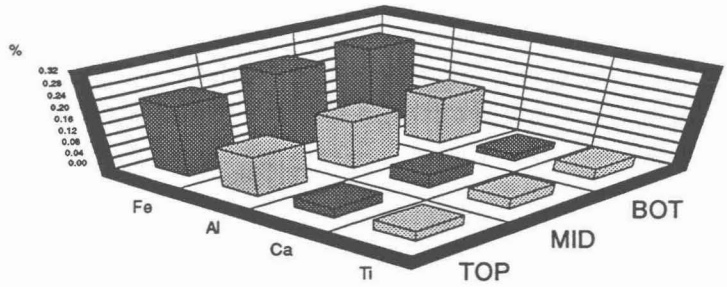

Fig 5. Minor element distribution in the vertical section of the cast, for major ladle additions, sample - T4M1

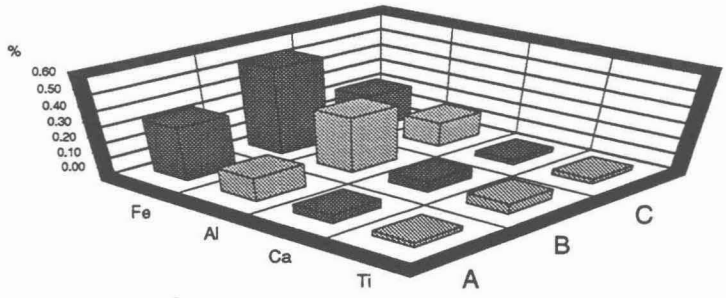

Fig 6. Minor element distribution, horizontally across the mould, sample T7M3

3. There was a definite concentration of intermetallics near gas voids, compared to other sections where there was a deficiency of voids. This association was not affected by cooling rate or whether additions were made to the silicon during refining. Generally, however, there seemed to be a higher concentration of these voids in samples subject to minor element additions. This phenomenon is shown in Plate 1 where aluminium and limestone were added to the ladle. There was also a higher frequency of intermetallics in samples where additions were made as a result of the higher concentration of minor elements in these casts. This plate also illustrates that once away from these voids the intermetallics became "fine strands" associated with the grain boundaries.

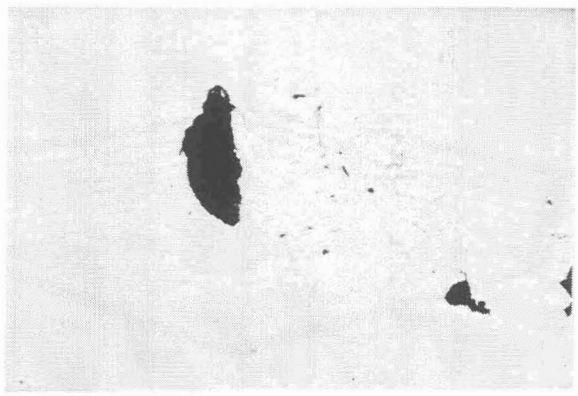

Plate 1. Gas void - intermetallic association in addition casts, sample T6M4

4. The intermetallics were not homogeneously distributed through the thickness of the silicon cast and were generally found to be concentrated at the centre and/or bottom of the cast, depending on whether additions were made or not. Plates 2, 3 and 4 are of a typical cross section through the thickness of a single cast where no additions were made.

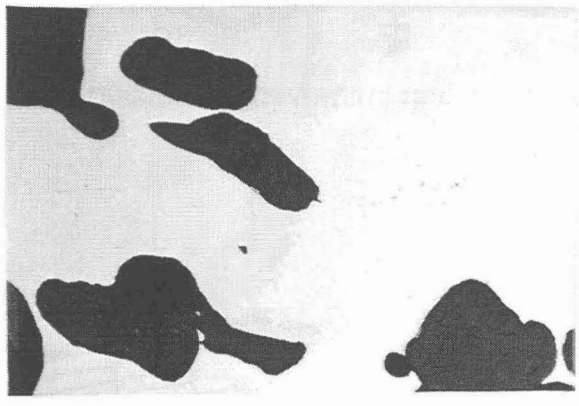

Plate 2. Gas void - intermetallic association in non-addition casts, top section of sample T5M3

5. There was a slight difference between the addition and non-addition micrographs. Generally, the intermetallics were concentrated in the centre of the cast for non-additions and concentrated in the middle and bottom sections for casts where additions had been made.

6. There were four major and several minor intermetallic phases which were visible using optical microscopy. The four major phases were identified and appear in decreasing abundance from a cream colour ($Si_5Al_7Fe_4$) to brown ($Si_{10}Al_8Fe_5Ca$) to gold (Si_2FeTi) to grey (Si). Plate 5 is an example of the variety of intermetallic phases which were observed.

7. There were three distinct types of intermetallic phases. The first was concentrated areas of intermetallics associated with gas voids. These can be relatively massive as shown in Plate 1. The second was associated with the grain boundaries and the

third appear to have precipitated out and "settled" during final crystallisation of the silicon. This latter type is shown in Plate 6, which displays the "trail" associated with each intermetallic particle. It is unknown whether this affect was due to gravity, diffusion or whether it is related to other factors. This particular phenomenon was found in casts for both addition and non-addition trials. It has also not been reported in the available literature on silicon structures. Further work is being undertaken to identify the possible mechanism of the formation of the trails, and the composition of the small intermetallic particles which display this characteristic.

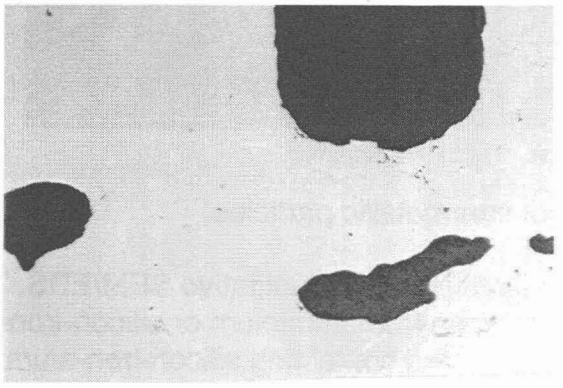

Plate 3. Middle section of the cast of sample T5M3

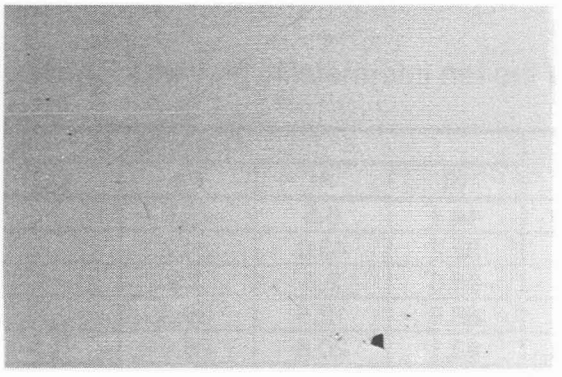

Plate 4. Bottom section of the cast of sample T5M3

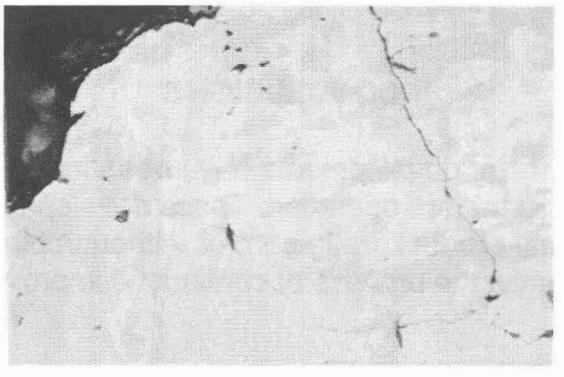

Plate 5: Section showing different intermetallic phases existing in sample T5M1

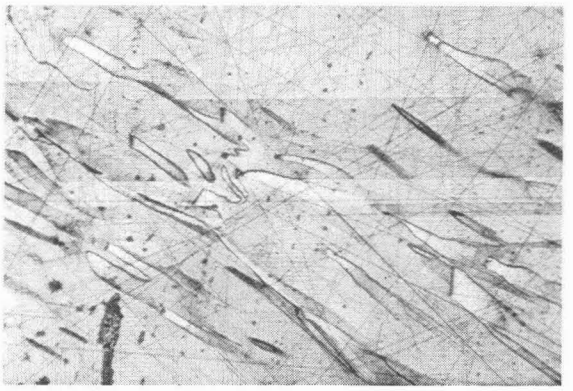

Plate 6. "Trail" features of intermetallic particles

8. Twenty phases were identified using qualitative SEM/EDS. The phases were mainly ternary containing silicon-iron-aluminium or silicon-iron-titanium. Two quaternary phases were identified containing silicon-iron-aluminium-titanium. No binary phases were identified. Ten of the phases were analysed quantitatively using SEM/EDS. The others were too small to allow quantitative analysis. The details of the ten phases identified are listed in Table 3. Si_2FeTi was the only phase previously published [6].

Table 3. Composition of the ten intermetallic phases identified in this study

Phases	Atomic %				
	Si	Al	Fe	Ca	Ti
$Si_{13}Al_2Fe_7Ti_7$	44.4	6.8	25.0		23.4
$Si_5Al_7Fe_4$	32.2	43.0	24.7		
Si	96.0	2.3	1.2		
$Si_9Al_2Fe_5$	56.6	12.5	30.6		0.1
$Si_9Al_4Fe_5$	48.1	20.6	26.0	0.1	3.1
$Si_{10}Al_8Fe_5Ca$	40.4	34.0	21.4	4.1	
Si_2FeTi	46.5	2.8	25.6		24.7
$Si_8Al_5Fe_5Ti_4$	36.5	23.2	22.4		17.8
$Si_8Al_{11}Fe_6$	31.8	43.5	24.4		0.1
$Si_5Al_2Fe_2$	44.2	36.4	19.3		

CONCLUSIONS

At Simcoa a number of major developments have been made in the short history of producing silicon at the Kemerton operation. These developments have been in the areas of both process and product grade control. Although plant efficiencies have been improved significantly, the process of continuous improvement in the plant is an ongoing one.

Simcoa places a high priority on reducing the variation in product analysis. This is being achieved by improved control of the process, raw materials, and, more recently, by the use of ladle additions.

Ladle additions do not appear to have any detrimental effect on the chemistry or microstructure of the cast silicon. The only difference observed was the increased proportion of intermetallics where additions were made. This is directly related to the increased concentration of minor elements as a result of these additions.

A number of observations were made which have not been previously reported in the published literature. These include the close association of gas voids or vesicles with intermetallics and the high concentration of intermetallics in the vicinity of these voids. Another previously unreported observation was the visible "trails" associated with some small intermetallics. At this stage the composition and the mechanism of formation of these "trails" are unknown. Work is continuing on both the chemistry and structure of these intermetallics and their associated "trails" in order to gain further knowledge regarding their formation, their distribution and their possible impact on the performance of Simcoa's silicon in the MCS process.

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