

Evaluation of silicon substituted *in situ* setting calcium phosphate cements

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Statement of Purpose: Silicon (Si) substitution in crystal structures of apatite has been a recent interest in orthopedic and dental applications. Natural bone is known to be low crystalline apatite with 4-6% carbonate [1] and ~0.1% silicon [2] substituted in the crystal structure. However, the most common methods in literature to synthesize Si substituted apatite materials involve high sintering temperatures, which produce high crystalline apatite structures without carbonate substitution. Therefore, in this study, we developed and evaluated several formulations of *in situ* setting calcium phosphate cements which would cure into carbonated apatite with silicon substitution under physiological conditions.

Methods: The *in situ* setting calcium phosphate cement contains two components: the powder component and the liquid component. The powder component contains α -tricalcium phosphate, calcium carbonate and monocalcium phosphate monohydrate. The liquid component contains dibasic sodium phosphate heptahydrate, monobasic sodium phosphate monohydrate and sodium silicate (Si-05-N and Si-10-N), or monobasic sodium phosphate monohydrate and sodium silicate (Si-05-A and Si-10-A). Five different formulations were evaluated in this study, including a control group without any sodium silicate in the liquid component.

The setting behavior of all formulations was evaluated using a modified Gilmore needle method. The powder and liquid components for each formulation were mixed to generate a paste, which was then cured in PBS (pH 7.4) at 37°C for 5, 10 and 15 min. An indenter was loaded 1.27 mm into the sample at rate of 15.24 mm/min.

The mineral phase of each formulation was evaluated using XRD and ATR-FTIR after the cements were cured in PBS (pH 7.4) at 37°C for 2 weeks. The molar ratios of Ca/P and Ca/(P+Si) in each formulation were calculated using the ion concentrations determined with ICP-OES. The inorganic carbonate content in each formulation was determined using a carbon coulometer equipped with an acidification unit.

Results / Discussion: All five formulations formed low crystalline apatite as determined by XRD spectra (Figure 1, where Si-10-N was used as an example to show comparison with the control group). ATR-FTIR also confirmed the apatite as the dominating phase in all formulations. The resultant apatites had Si contents ranging from 0.34 wt% to 0.70wt% as measured using ICP-OES (Table 2), indicating the incorporation of Si in the apatite structure has an efficiency ranged from 67% to 82% under the conditions in this study. The inorganic carbonate content for all five formulations ranged from 5.4 wt% to 5.6wt% as determined by carbon coulometry. The setting behaviors evaluated by the indentation study revealed that the addition of silicate solution in the liquid component of the reaction decreased the indentation

force, indicating longer setting time was required for the hydraulic reaction with silicate.

Table 1. Compositions of Different Formulations

Sample	Theoretical Si content	Si by ICP	Theoretical Ca/P	Actual Ca/P	Theoretical Ca/(Si+P)	Actual Ca/(Si+P)
Control	N/A	0.01%	1.67	1.63	N/A	1.63
Si-05-N	0.50%	0.41%		1.69	1.60	1.65
Si-10-N	1.00%	0.70%		1.76	1.56	1.68
Si-05-A	0.50%	0.34%		1.63	1.60	1.59
Si-10-A	1.00%	0.67%		1.66	1.56	1.59

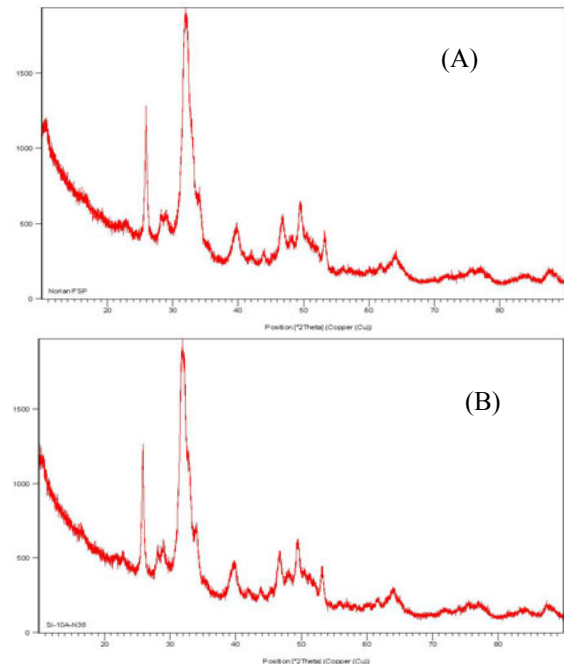


Figure 1. XRD spectra of cured apatite: (A) control group; (B) Si-10-N formulation.

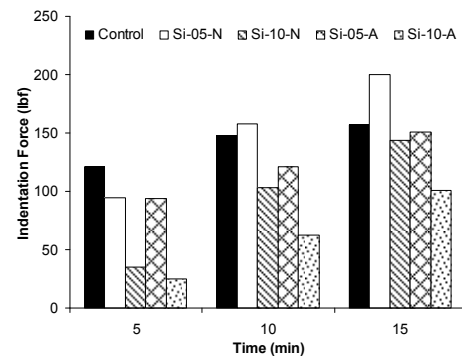


Figure 2. Indentation force of five formulations

Conclusions: The hydraulic cement formulations in this study cured into low crystalline apatite with 5.4wt% to 5.6wt% carbonate and 0.34wt% to 0.70wt% silicon substitution under physiological conditions, and thus showed their potential as bone graft materials.

References:

1. Iso IC, Fulmer MT, Barr BM, Constantz BR, Hydroxyapatite and Related Materials, 215-224 (1994).
2. Carlisle EM, Science, 167 (3916): 279-280 (1970).