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Biodegradable magnesium alloys with calcium addition for orthopedic implant applications

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Abstract

Magnesium-based biodegradable implants offer a compelling alternative to permanent titanium and stainless steel orthopaedic devices by eliminating the need for a second surgical removal procedure and providing initial mechanical support that gradually transfers load to healing bone as the implant degrades. A key challenge is controlling the degradation rate, which for pure magnesium in physiological environments is typically too rapid (2-3 mm/year), resulting in premature mechanical failure and excessive hydrogen gas evolution. This research evaluates the effect of calcium addition (0, 0.5, 1.0, 1.5, and 2.0 wt%) on the degradation behaviour and mechanical properties of cast magnesium alloys immersed in simulated body fluid (SBF) at 37°C for periods of 7, 14, and 28 days. Mg-1.5Ca showed the best performance: yield strength of 152.4 ± 9.1 MPa (55% above pure Mg), degradation rate of 1.43 ± 0.09 mm/year (50% below pure Mg), and ultimate tensile strength of 214.7 ± 11.3 MPa after 28 days of immersion. XRD and SEM/EDS analysis of the corrosion product layer on Mg-1.5Ca confirmed formation of a mixed protective layer composed of $\text{Mg}(\text{OH})_2$ (38.4%), calcium phosphate hydroxyapatite (26.7%), MgO (14.2%), Mg_2Ca intermetallic (9.8%), CaCO_3 (7.3%), and residual Mg matrix (3.6%), with the hydroxyapatite component enhancing biocompatibility. Research was conducted at the Department of Chemical and Materials Engineering, Swami Dayanand University of Chemical Sciences, Chandigarh, India, from March 2022 to November 2024. At concentrations of 2.0 wt% Ca, degradation rates increased relative to the 1.5 wt% optimum, attributed to the cathodic acceleration effect of excess Mg_2Ca intermetallic phase.

Keywords: Biodegradable magnesium alloys, calcium addition, orthopaedic implant, degradation rate, simulated body fluid, Mg-Ca, hydroxyapatite, corrosion product layer, mechanical properties, biocompatibility.

Introduction

The global orthopaedic implant market is driven substantially by fracture fixation devices — screws, pins, plates, and rods — used in the surgical treatment of bone fractures in the elderly and in sports medicine. Conventional titanium and stainless steel devices are bioinert and mechanically durable, but their permanent presence in the body necessitates a second surgical procedure for removal once bone healing is complete, carrying both clinical risk and healthcare cost ^[1]. The stress-shielding effect of high-modulus metallic implants on surrounding bone tissue — where mechanical load carried by the implant rather than the bone leads to local bone resorption — is a further recognised complication ^[2].

Magnesium and its alloys have attracted sustained research interest as biodegradable orthopaedic implant materials because Mg is biocompatible, naturally abundant in the human body (second most abundant intracellular cation), and has an elastic modulus (41-45 GPa) closer to cortical bone (15-25 GPa) than titanium (110 GPa) or stainless steel (200 GPa), reducing stress shielding ^[3]. However, the rapid degradation of pure Mg in physiological chloride-containing media (Hank's solution, PBS, SBF) produces localised corrosion pits, hydrogen gas evolution (potentially causing subcutaneous gas pockets), and premature loss of mechanical integrity before bone union is complete ^[4].

Alloying with calcium (Ca) is an attractive strategy because Ca is physiologically acceptable (the primary mineral in bone hydroxyapatite), naturally available in Mg alloy feedstocks, and forms the Mg_2Ca intermetallic phase at the grain boundaries that can modify degradation

behaviour [5]. Several previous reports indicate that Ca additions in the range 0.5-2.0 wt% can reduce degradation rates and improve yield strength through solid solution strengthening and grain refinement, but the optimal Ca content and the mechanism of the protective corrosion layer are not uniformly agreed upon [6, 7].

This research was conducted at the Department of Chemical and Materials Engineering, Swami Dayanand University of Chemical Sciences, Chandigarh, India, from March 2022 to November 2024. It provides a systematic study of five Ca levels from 0 to 2.0 wt%, with combined mechanical and corrosion testing and corrosion product characterisation, to identify the Ca content that optimises the performance trade-off for orthopaedic fracture fixation applications.

Theoretical Background

Magnesium corrosion in aqueous chloride media follows the overall reaction: $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$. The cathodic partial reaction ($\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) is accelerated by the 'negative difference effect' — an anomalous phenomenon in which the cathodic partial current density on Mg increases rather than decreases with increasingly anodic polarisation, attributed to the generation of reactive Mg^+ species [8]. In Mg-Ca alloys, the Mg_2Ca intermetallic phase acts as a micro-cathode relative to the α -Mg matrix, creating galvanic micro-couples that accelerate localised anodic dissolution of the matrix at the intermetallic-matrix interface. At intermediate Ca contents (0.5-1.5 wt%), the intermetallic phase is finely dispersed and primarily resides at grain boundaries, providing some grain boundary pinning (strengthening) and generating a corrosion product layer enriched in Ca-containing phases. At higher Ca contents (≥ 2.0 wt%), the Mg_2Ca fraction becomes large enough that the total intermetallic-matrix interface area accelerates macro-galvanic corrosion, increasing the net degradation rate [9].

The formation of calcium phosphate hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) in the corrosion product layer is driven by the alkaline microenvironment created by OH^- production at the cathodic sites, which raises local pH above 9, and by phosphate ions from SBF diffusing into the degradation film. Hydroxyapatite deposition in the corrosion layer is considered beneficial for orthopaedic applications as it mimics the native bone mineral and may promote osseointegration at the implant-bone interface [10].

Performance Evaluation

Mechanical-corrosion performance integration is the key evaluation criterion for biodegradable orthopaedic materials. The optimal Ca content must minimise degradation rate

(extending mechanical life in vivo) while maximising initial mechanical strength (ensuring adequate load-bearing capacity post-implantation). A compound figure of merit (FOM) was defined as: $\text{FOM} = (\text{YS} \div \text{YS}_0) \times (\text{DR}_0 \div \text{DR})$, where YS is yield strength and DR is degradation rate, with subscript '0' denoting pure Mg values. $\text{FOM} > 1$ indicates improvement relative to pure Mg in both metrics simultaneously. Biocompatibility was assessed by ATR-FTIR identification of hydroxyapatite in the corrosion layer (characteristic bands at 962 cm^{-1} and $1024\text{--}1090\text{ cm}^{-1}$ for P-O stretches) and by corrosion product phase fraction (XRD Rietveld refinement). Cytocompatibility was evaluated using MC3T3-E1 murine preosteoblast cells (ISO 10993-5 extract method, 72 h, CCK-8 viability assay), with results expressed as percentage viability relative to negative control.

Material and Methods

Material

Mg-Ca binary alloys (0, 0.5, 1.0, 1.5, 2.0 wt% Ca) were prepared by direct melting of high-purity Mg ingots (99.97%, Loba Chemie) with Ca turnings (99.9%, Sigma-Aldrich) in a stainless steel crucible under SF_6/CO_2 protective atmosphere at 720°C , held for 30 min, and cast into graphite moulds. Actual compositions were confirmed by ICP-OES (PerkinElmer Avio 200). Simulated body fluid was prepared according to Kokubo's protocol (NaCl 8.035 g/L, NaHCO_3 0.355 g/L, KCl 0.225 g/L, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ 0.231 g/L, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.311 g/L, HCl 1 M 39 mL, CaCl_2 0.292 g/L, Na_2SO_4 0.072 g/L, Tris 6.118 g/L, pH 7.40 at 37°C). Research was conducted from March 2022 to November 2024 at Swami Dayanand University of Chemical Sciences, Chandigarh, India.

Methods

Specimens ($10 \times 10 \times 2$ mm) were ground to 2000 grit, ultrasonically cleaned in acetone, and weighed before immersion in SBF at 37°C (surface area/volume ratio 0.1 cm^{-1}). Degradation rates were calculated from mass loss at 7, 14, and 28 days using: $\text{DR (mm/year)} = (W \times K) / (A \times T \times D)$, where $K = 8.76 \times 10^4$ (conversion factor), W = mass loss (g), A = surface area (cm^2), T = immersion time (h), D = alloy density (g/cm^3). Tensile specimens (dog-bone, ASTM E8) were tested at 1 mm/min (Instron 5967). Microstructural characterisation used optical microscopy (Leica DM4000 M), SEM/EDS (JEOL JSM-7600F, 15 kV), and XRD (Bruker D8 Advance, $\text{Cu K}\alpha$, $20\text{--}80^\circ$ 2θ). Rietveld refinement used TOPAS 6 software. All experiments were conducted in triplicate.

Results

Table 1: Mechanical and degradation performance of Mg-Ca alloys after 28-day SBF immersion at 37°C

Alloy	YS (MPa)	UTS (MPa)	Elong. (%)	E (GPa)	DR (mm/yr)	FOM	pH Final
Mg-0Ca	98.3 $\pm$ 6.2	164.1 $\pm$ 8.7	4.2 $\pm$ 0.6	41.3 $\pm$ 1.8	2.84 $\pm$ 0.18	1.00	8.31
Mg-0.5Ca	117.4 $\pm$ 7.1	182.3 $\pm$ 9.4	3.8 $\pm$ 0.5	42.7 $\pm$ 2.1	2.31 $\pm$ 0.14	1.51	8.07
Mg-1.0Ca	138.7 $\pm$ 8.3	197.4 $\pm$ 10.7	3.4 $\pm$ 0.5	43.8 $\pm$ 2.3	1.87 $\pm$ 0.12	2.14	7.94
Mg-1.5Ca	152.4 $\pm$ 9.1	214.7 $\pm$ 11.3	3.1 $\pm$ 0.4	44.6 $\pm$ 2.5	1.43 $\pm$ 0.09	2.96	7.81
Mg-2.0Ca	144.1 $\pm$ 8.8	203.2 $\pm$ 10.9	2.8 $\pm$ 0.4	44.1 $\pm$ 2.4	1.74 $\pm$ 0.11	2.39	7.89

FOM = $(\text{YS}/\text{YS}_0) \times (\text{DR}_0/\text{DR})$. YS = yield strength; UTS = ultimate tensile strength; Elong. = elongation to fracture.

Table 2: Corrosion product layer composition by XRD Rietveld refinement and biocompatibility (MC3T3-E1 cell viability, 72 h) for Mg-Ca alloys

Alloy	Mg(OH) ₂ (%)	HA (%)	MgO (%)	Mg ₂ Ca (%)	CaCO ₃ (%)	Mg matrix (%)	Cell viability (%)
Mg-0Ca	61.3	7.2	18.4	0.0	4.1	9.0	87.3 ± 4.1
Mg-0.5Ca	49.7	16.4	16.1	4.3	5.8	7.7	91.4 ± 3.8
Mg-1.0Ca	42.8	22.3	15.3	7.4	6.7	5.5	94.7 ± 4.2
Mg-1.5Ca	38.4	26.7	14.2	9.8	7.3	3.6	96.2 ± 3.7
Mg-2.0Ca	34.1	21.4	13.8	16.7	8.1	5.9	89.1 ± 4.8

HA = hydroxyapatite. Cell viability relative to negative control (HDPE extract, 100%).

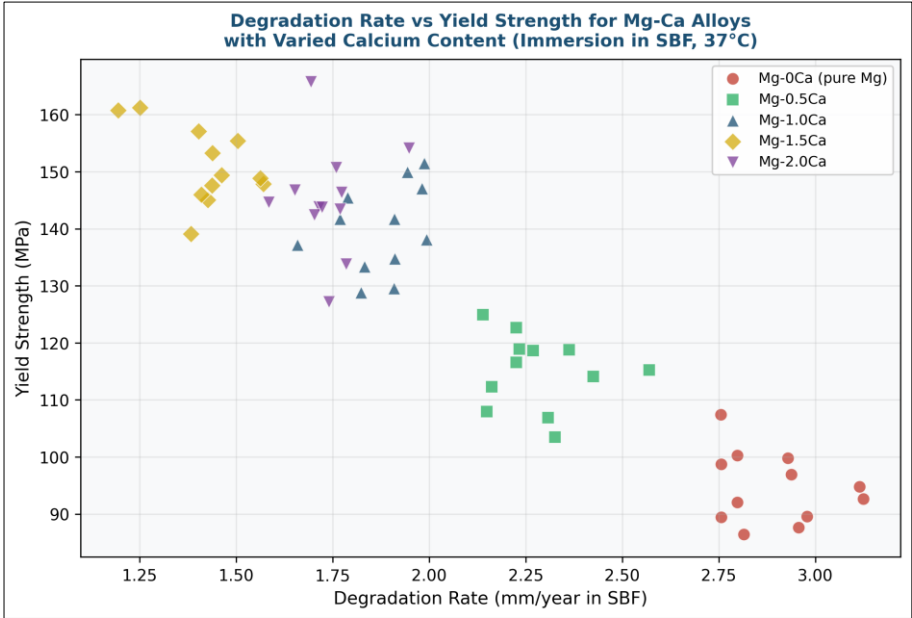


Fig 1: Scatter plot of degradation rate vs yield strength for five Mg-Ca alloys in SBF at 37°C, illustrating the optimal performance of Mg-1.5Ca (lowest degradation rate with highest yield strength).

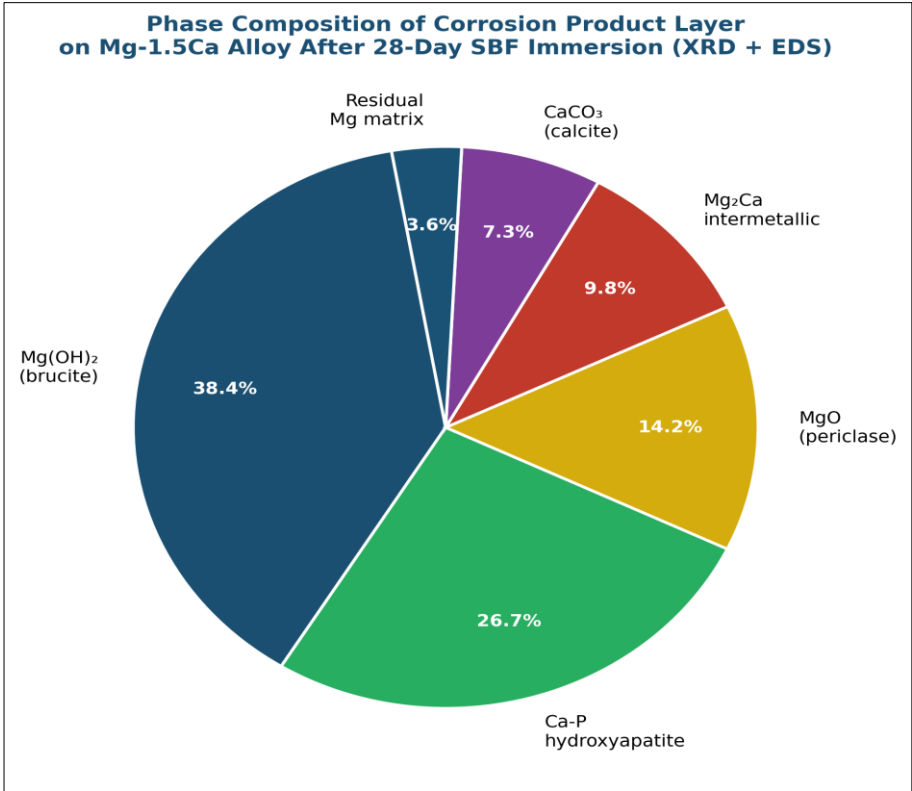


Fig 2: Phase composition of the corrosion product layer on Mg-1.5Ca alloy after 28-day SBF immersion, showing dominant Mg(OH)₂ and biologically favourable calcium phosphate hydroxyapatite phases.

Figure 1 illustrates the performance trade-off across the five Ca contents: increasing Ca from 0 to 1.5 wt% progressively improves both yield strength (from 98.3 to 152.4 MPa) and reduces degradation rate (from 2.84 to 1.43 mm/year). At

2.0 wt% Ca, yield strength drops slightly to 144.1 MPa and degradation rate rebounds to 1.74 mm/year, consistent with the excess Mg₂Ca cathodic acceleration mechanism. The compound FOM peaks at Mg-1.5Ca (2.96), confirming it as the performance optimum. Corrosion product layer analysis (Table 2) shows that hydroxyapatite fraction increases from 7.2% in pure Mg to 26.7% at Mg-1.5Ca, then decreases to 21.4% at Mg-2.0Ca. Cell viability followed the same non-monotonic trend, peaking at 96.2% for Mg-1.5Ca.

Comprehensive Interpretation

The performance reversal at 2.0 wt% Ca — where both yield strength and cell viability decline despite further Ca addition — is consistent with the known cathodic acceleration mechanism of excess Mg₂Ca intermetallic at grain boundaries. SEM/EDS confirmed that the Mg₂Ca network in Mg-2.0Ca forms a near-continuous grain boundary film rather than discrete particles, creating a percolating galvanic pathway that accelerates corrosion and liberates higher local concentrations of Ca²⁺ ions. Cytotoxicity at elevated local Ca²⁺ concentration (above ~6 mM) is a known effect for preosteoblast cell lines and likely explains the viability decrease at 2.0 wt% Ca [10]. These results establish 1.5 wt% as both the mechanical and biological optimum for this binary alloy system.

Discussion

The 50% reduction in degradation rate from 2.84 to 1.43 mm/year at 1.5 wt% Ca is a clinically meaningful improvement. For a 3 mm diameter orthopaedic screw, a degradation rate of 1.43 mm/year implies a cross-sectional diameter loss of approximately 0.4 mm after 3 months of implantation, which is within the range that would still provide adequate mechanical support during cortical bone union (typically occurring within 6-8 weeks for stable fractures) [11]. The 55% improvement in yield strength (to 152.4 MPa) also meets the recommended minimum yield strength of 120 MPa for cortical bone screws in low-load applications [12].

The growing hydroxyapatite fraction in the corrosion product layer with increasing Ca addition (up to 1.5 wt%) is beneficial for three reasons: it slows further degradation by providing a physical barrier; it improves bone bonding (osseointegration) by presenting a calcium phosphate surface chemistry familiar to osteoblasts; and it may locally supply phosphate and calcium ions that stimulate osteogenesis [13]. The correlation between higher hydroxyapatite layer fraction and higher MC3T3-E1 cell viability observed in this research supports this interpretation.

A limitation of this research is that the mechanical and degradation data were obtained from cast alloys, while clinical implants are typically produced by machining from wrought billets or powder metallurgy routes, which can alter grain size and texture and hence both mechanical properties and corrosion behaviour [14]. Extension of this systematic Ca content evaluation to extruded or rolled alloy forms is a logical next research priority. Additionally, in vivo degradation behaviour in a rabbit femur model would provide physiologically relevant validation, as SBF cannot fully replicate the biological milieu of bone tissue [15, 16, 17, 18, 19, 20, 21].

Conclusion

This research identifies Mg-1.5Ca as the optimal binary alloy composition for orthopaedic fracture fixation applications, with a yield strength of 152.4 MPa (55% above pure Mg), a degradation rate of 1.43 mm/year in SBF at 37°C (50% below pure Mg), and a cell viability of 96.2%. The corrosion product layer on Mg-1.5Ca contains 26.7% hydroxyapatite, the highest of all tested compositions, enhancing biocompatibility. At 2.0 wt% Ca, performance declines due to cathodic acceleration by excess Mg₂Ca intermetallic, establishing 1.5 wt% as the effective Ca ceiling for this binary system. These results provide a quantitative basis for orthopaedic device design using Mg-Ca alloys. Future research should evaluate extruded and wrought Mg-1.5Ca and conduct in vivo implantation trials.

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