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Evaluation of long-term durability of slag-treated clay under seawater exposure

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ABSTRACT

The large amounts of dredged clay acquired through dredging work to maintain water depths have become problematic problem in the coastal areas of Japan. In addition, approximately 38 million tons of steel-making slag are produced annually in Japan. It is commonly believed that deterioration due to seawater exposure occurs due to the ion exchange between the calcium in cement-treated clay and the magnesium in seawater. In this study, we evaluated the long-term durability of slag-treated clay compared to cement-treated clay. Unconfined compressive tests demonstrated that the strength increment ratio of post-exposure to pre-exposure of slag-treated clay was higher than that of the cement-treated clay. However, the ion exchange rate of the slag-treated clay was more often higher than cement-treated clay. This result implies that, compared to the cement-treated slag, the slag-treated clay has a different deterioration and self-mediated mechanism.

Keywords: steel-making slag, cement, dredged clay, durability, seawater exposure

1 INTRODUCTION

Japan produces approximately 38 million tons of steel-making slag annually. Steel-making slag is a by-product of steel-making and is considered an environmentally friendly material. It has traditionally been used as a roadbed material and in cement; however, slag is now used in a wide range of applications (Horii et al., 2012). For example, steel-making slag is used as geomaterial in the construction of ports. In the past, natural materials, e.g., mountain sand, and sea sand, have been used in landfills and construction tidelands (Yamakoshi et al., 2014); however, collecting natural sand has been prohibited in many prefectures (Takeoka et al, 2005). As a substitute material, slag-treated clay has been applied to port construction, which helps reuse resources, and solve problems in coastal areas, such as a lack of landfill sites and the restriction on the collecting of natural resources.

Many researchers have studied slag-treated clay, and it has been reported that the solidification mechanism of slag can be classified as water absorption and hydration reaction (Yamakoshi et al., 2014). Water absorption occurs immediately after mixing, and the hydration reaction occurs between the silica or aluminum in both the clay and calcium in slag. Here, calcium silicate hydrate (C-S-H) or calcium aluminate hydrate is formed, which contributes to solidification. Cikmit et al. (2017) suggested that the strength increment process is divided into three periods, i.e., the preparation of the strength development period (within the first five hours of curing), the early strength development period (from five to 72 hours of curing), and the late strength development period (after 72 hours of curing). Sato et al. (2018) reported that the strength of slag-treated clay increased as the particle size of the slag became smaller. Other studies have focused on the chemical compositions in dredged clay. When focusing on controlling the components in dredged clay for C-S-H formation, one factor that affects strength development is the amount of amorphous silica, which is the most reactive of the silica-bearing phases in dredged clay (Toda et al., 2018). In addition, the shear strength of dredged clay containing amorphous silica from diatoms develops earlier than that from minerals, and the difference in the development of shear strength can be attributed to the difference in the origin of the amorphous silica (Kakihara et al., 2020).

Many studies that investigated slag-treated clay focused on the strength development, and, to the best of our knowledge, fewer studies have focused on the deterioration mechanism under seawater exposure. Nevertheless, slag-treated clay is frequently applied to port construction. Hara et al. (2013) conducted an exposure test to artificial seawater to investigate the deterioration mechanism of cement-treated soil. They found that calcium ions in the cement-treated soil were leached by the salt containing magnesium ions in seawater. Here, calcium ion elution caused disintegration of cementation substances, e.g., C-S-H, which led to mechanical deterioration. In addition, one of the countermeasure methods to prevent elution of calcium ions promotes reprecipitation into the specimens based on the microbial function. it can maintain stable conditions, which can promote the use of cement-treated clay under the seawater exposure conditions (Hata et al., 2020). Thus, deterioration mechanisms must be elucidated and countermeasures must be developed to promote the use of steel slag-treated clay in coastal construction projects.

Therefore, in this study, we evaluated the long-term durability of slag-treated clay compared to cement-treated clay. Here, unconfined compressive tests were conducted on specimens exposed to artificial seawater for 28–90 days. In addition, the balance of ions in the specimen was studied by measuring the calcium and magnesium ions in exposed seawater.

2   MATERIALS

2.1   Dredged clay

The dredged clays used in this study were collected from three different locations in the Seto Inland Sea, Japan. In this paper, we refer to the collected samples as Clay A, Clay B, and Clay C. The physical properties of the dredged clays are listed in Table 1. In this study, the test method for the liquid and plastic limits conforms to JGS 0141-2009. JGS implies the standard defined by Japan Geotechnical Society. Note that clay A was classified as high liquid limit silt, and Clays B, and C were classified as high liquid limit clays. The elemental compositions of the samples, which were determined using an X-ray fluorescence technique, are shown in Table 2. Note that a 2-mm sieve was utilized to remove shells from the clay samples, and the result shown in Table 2 is not oxide form.

2.2   Binder

Two binders were used in this study, i.e., ordinary Portland cement and converter steel-making slag. The converter steel-making slag was obtained from an ironworks in Japan, and its physical properties are listed in Table 3. The elemental compositions of the cement slag are shown in Table 4. The particle size of the slag was less than 850 μm because the hydration reaction was promoted as the particle size decreased. The particle size distribution of the clay samples and slag are shown in Figure 1.

Table 1. *Physical properties of dredged clays*

Clay	Particle density (g/cm^3)	w_L (%)	w_P (%)	I_p	Classification	IL (%)
Clay A	2.59	52.9	31.7	21.2	MH (F-S)	6.6
Clay B	2.50	98.2	36.7	61.5	CH (F)	13.8
Clay C	2.60	128.7	36.9	91.8	CH (F)	10.1

Table 2. *Elemental compositions of dredged clays (unit: %)*

Clay	Si	Al	Ca	Fe	K	Cl	Others
Clay A	47.3	15.2	13.0	9.6	6.6	6.1	2.1
Clay B	42.1	12.8	10.3	12.6	5.4	13.9	2.9
Clay C	55.3	8.4	4.1	20.3	7.6	0.0	4.5

Table 3. *Physical properties of slag*

Type of slag	Converter steel-making slag
Density in saturated surface-dry condition (g/cm³)	3.18
Density in oven-dry condition (g/cm³)	3.05
Rate of water absorption (%)	4.16
Particle size	Less than 850 μm
Rate of free lime (%)	6.02

Table 4. *Elemental compositions of binders (unit: %)*

Binder	Ca	Fe	Si	Mn	S	Others
Slag	59.5	30.7	6.4	2.2	0.0	1.2
Cement	83.1	4.7	9.2	0.0	1.2	1.6
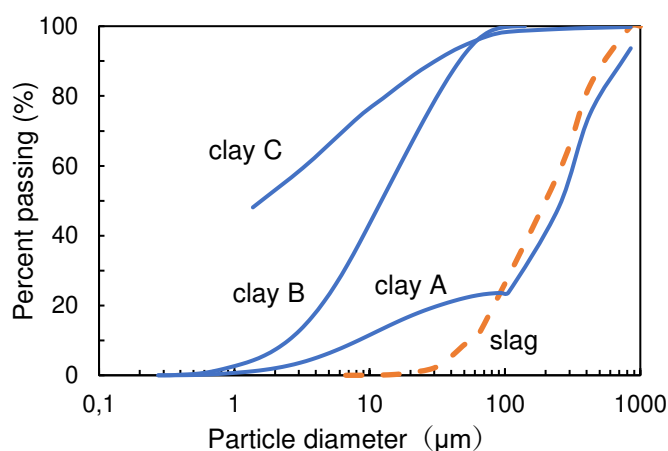
Figure 1. *Particle size accumulation curve*

3 METHODOLOGY

3.1 Preparation of specimens

The test conditions are shown in **Table 5**. In this study, the mixing ratio of the dredged clays and binders was clay : slag = 100 : 30 and clay : cement = 100 : 8 by weight. The adding ratios of slag and cement were equivalent to 10% by volume and 100 kg/m³, respectively, and each binder was added to the wet clay.

The specimens were prepared as follows. The water content of each clay was set to 1.5 times the liquid limit. Here, artificial seawater was used to adjust the water content. The prescribed amounts of clay and binder were mixed for five minutes using a hand mixer. Then, the mixture was packed into a plastic mold while eliminating the air. The diameter and height of the mold were 35 mm and 80 mm, respectively. The packed mixtures in molds were tightly sealed and cured at a constant temperature of 20℃ for 28 days. After curing, one-third of the specimens were used for unconfined compressive tests. The test method conforms to JGS 0511-2009. The rest of the specimens were exposed to the artificial seawater.

3.2 Exposure to artificial seawater

The exposure to artificial seawater test was conducted as follows (Ikoma et al., 2021). After curing, two-thirds of the specimens were covered on the sides by a rubber membrane, the bottom was covered by Parafilm, and the top surface was left exposed so that the degradation of the specimens progressed unidirectionally. After the specimens were prepared, they were placed in a vessel filled with 150 ml of artificial seawater. Here, plastic wrap was used to seal the openings off the vessel to prevent evaporation. The exposure was conducted in a constant temperature chamber at 30℃ for 28 days or 90 days. During

exposure, the seawater was sampled, and exchanged every two weeks. The process used to prepare the specimens for the exposure test is illustrated in Figure 2. Unconfined compressive tests were conducted after the prescribed curing time. Here, the membranes were not removed to avoid disarranging the specimens. The strength difference between the wrapped and unwrapped specimens was compared to evaluate the effect of the membrane on the strength of the specimen. The results demonstrate that the effect of the membrane was negligible and could be ignored.

In addition, the total amount of ions contained in the sampled seawater was measured. According to a previous study, specimens exposed to seawater degrade due to the exchange of calcium and magnesium (Hara et al., 2013); thus, we expect that the deterioration mechanism of slag-treated clay can be revealed by measuring the amount of calcium ion elution from a specimen to seawater and magnesium ion absorption to a specimen. The sampled seawater was diluted to 10 times and filtered using a 0.2-μm millipore filter. Then, the ion concentration was measured using a portable absorption spectrophotometer (HANNA instruments; model number: HI 97752).

Table 5. *Test conditions*

Case	Clay	Binder	Clay content (%)	Binder content (%)
1 (A-8%cem)	Clay A	Cement	100	8
2 (B-8%cem)	Clay B	Cement	100	8
3 (C-8%cem)	Clay C	Cement	100	8
4 (A-30%sl)	Clay A	Slag	100	30
5 (B-30%sl)	Clay B	Slag	100	30
6 (C-30%sl)	Clay C	Slag	100	30
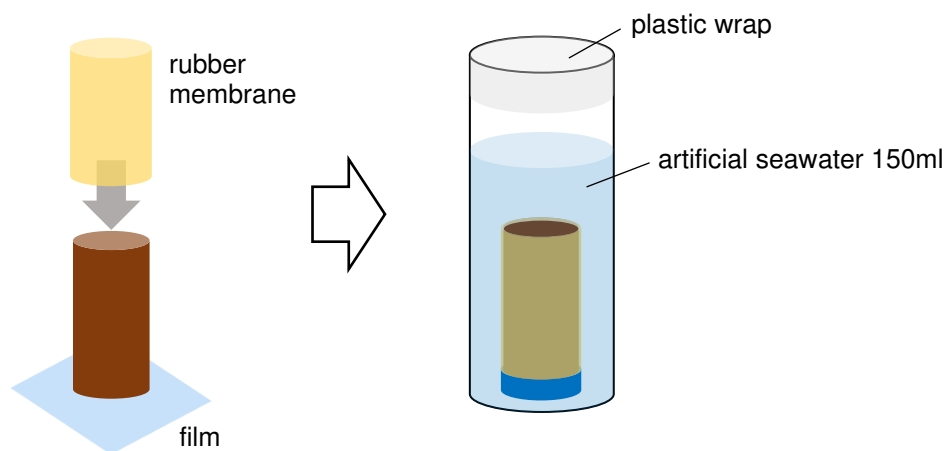
Figure 2. *Process of preparation the specimens for exposure test*

4 RESULTS AND DISCUSSIONS
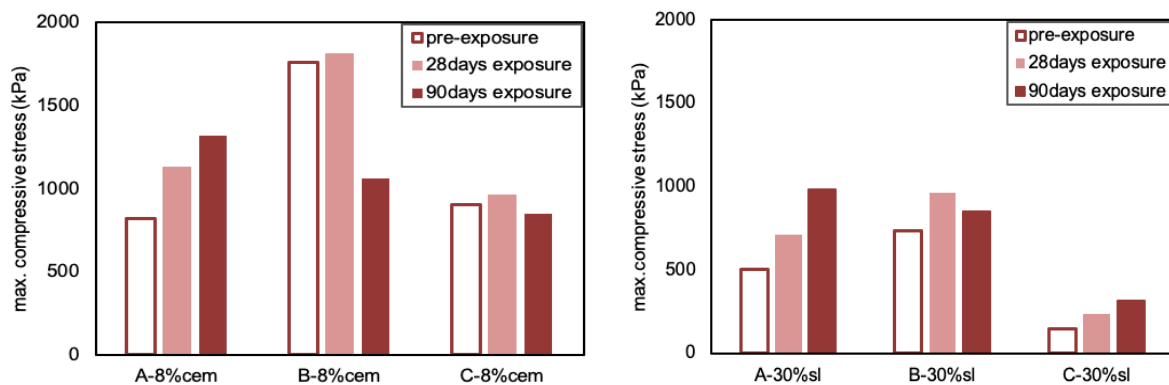
4.1 Unconfined compressive strength

Figure 3 shows the results of the unconfined compressive tests, and Table 6 shows the stress increment rate. Note that the maximum compressive stresses of pre-exposure and after 28 and 90 days of exposure are denoted q_0, q_{28}, and q_{90}, respectively. For the cement-treated clay, the stress values for cases 2 and 3 decreased after 90 days of exposure. For the slag-treated clay, only case 5 had lower q_{90} than q_{28} values; however, the q_{90} value was higher than the pre-exposure stress value (q_0).

The stress values of cases 1 and 4 (containing clay A) increased steadily. Prior to exposure, case 1 exhibited the least stress; however, this case demonstrated the most stress after 90 days of exposure. The cases with clay B exhibited reduced stress. This was particularly evident with case 2, which

deteriorated rapidly between 28 and 90 days of exposure. The stresses of case 3 fluctuated within narrow limits. For case 6, the stress before exposure was very low; however, the stress value increased steadily under the seawater exposure conditions. The rapid stress increase in the cases composed of clay was due to the high content of silica, alumina, and calcium. According to a previous study, the strength of slag-treated clay used in dredged soils containing amorphous silica from diatoms and minerals develops earlier than that of slag-treated clay composed of dredged soils containing amorphous silica from minerals (Kakihara et al., 2020). In the current study, the stress of the mixtures composed of clay B developed the earliest; thus, it is considered that clay B contained more amorphous silica from diatoms than other clays, which enabled an early hydrate reaction and caused rapid degradation after exposure.

To elucidate the origin of the silica, the soil particles were observed using an optical microscope. Figure 4 shows the results of microscopic observations. Here, we found that clays A and B contained two kinds of diatoms, and clay C contained only one type. In addition, the most diatoms were observed in clay B, which can be attributed to the high stress values. Many smaller minerals, approximately 20 μm in diameter, were scattered throughout clay A. Thus, the larger the specific surface area of the minerals, the more amorphous silica elutes. As a result, the cases mixed with clay A stabilized during the test period. These results confirm that the origin of silica in the clay is associated with long-term durability under seawater exposure.

In addition, with the cement-treated clay cases where q_{28}/q_0 was small, q_{90}/q_{28} was also small. Thus, a mechanical degradation of the specimens after 90 days of seawater exposure can be expected (as observed). These results suggest that the UCS strength gradually decreases in this period. Therefore, the unconfined compressive strength test can be used to determine the durability of specimens exposed to seawater for 28 and 90 days at 30℃. However, in this study, only one binder combination ratio was considered; thus, it attention should be paid to the term of exposure to estimate whether long-term durability changes depending on the mixing ratio.

Figure 3. *Results of unconfined compressive tests*

Table 6. *Rate of stress increment*

Case	q_{28}/q_0	q_{90}/q_0	q_{90}/q_{28}
1 (A-8%cem)	1.38	1.60	1.16
2 (B-8%cem)	1.03	0.61	0.54
3 (C-8%cem)	1.07	0.94	0.88
4 (A-30%sl)	1.42	1.96	1.45
5 (B-30%sl)	1.30	1.16	0.89
6 (C-30%sl)	1.58	2.13	1.35

clay A

0　　　　　50μm

clay B
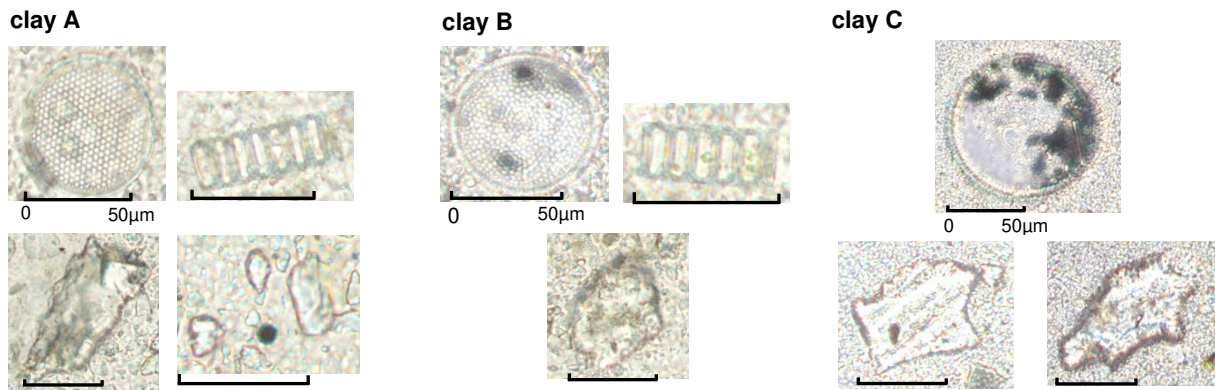

0　　　　　50μm

clay C

0　　　　　50μm

Figure 4. Observation of soil particle (upper row: diatoms, bottom row: minerals)

4.2　Measuring calcium elution and magnesium absorption

Figures 5 and **6** show the total amount of calcium ion elution and magnesium ion absorption after 28 and 90 days of exposure, respectively. In the cement-treated clay, calcium ions leaked the most from case 2, which may have hindered the strength increase under exposure to seawater. The stress increase rate shown in **Table 6** was reduced as the amount of calcium elution (**Figure 5**) increased. In contrast, there was no relationship between the rate of stress increase and magnesium absorption. As shown in **Figure 6**, after 90 days of exposure, both the calcium elution and magnesium absorption were related to q_{90}/q_0. In the slag-treated clay, calcium elution did not vary with the clay type; however, calcium elution did vary with the cement-treated clay. In addition, the magnesium absorption was greater in the order of clay A, clay B, and clay C. Thus, under our experimental conditions, it was difficult to determine whether the durability of the slag-treated clay is related to the ion exchange.

Slag-treated clay may have a different deterioration mechanism because it exhibits a different trend compared to the cement-treated clay. The fact that the calcium ion elution of the cement-treated clay was less than that of the slag-treated clay at a higher strength under seawater exposure also represents a difference in the deterioration mechanism.

In addition, after 28 days of exposure, the magnesium absorption was greater than the calcium elution in most cases; however, after 90 days, the calcium elution was greater than the magnesium absorption in all cases. Thus, we consider that the specimens absorbed magnesium ions from seawater to form $Mg(OH)_2$, after which calcium ions leaked from specimens. Note that the ion exchange does not occur simultaneously.
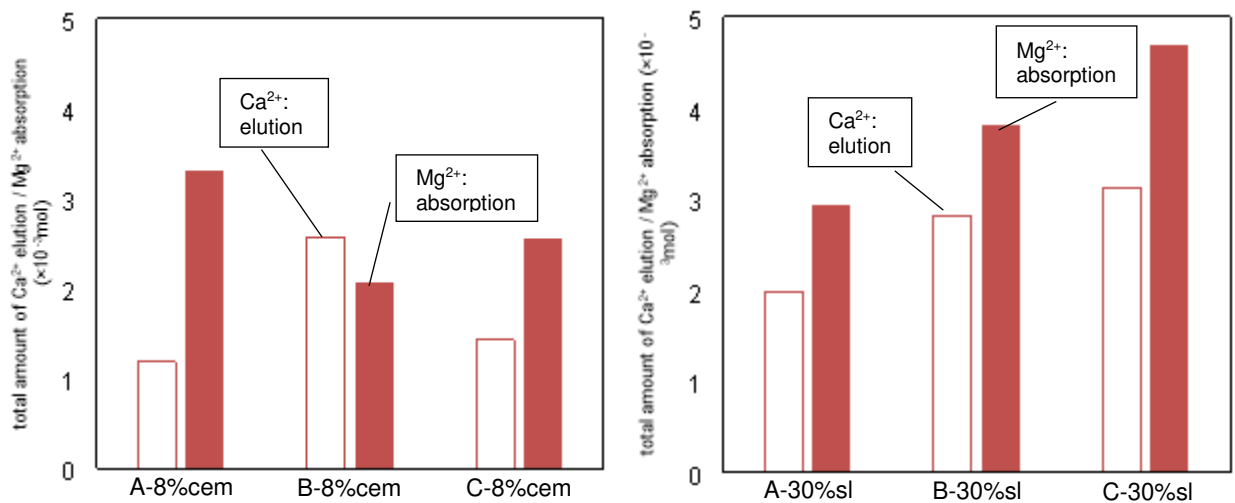

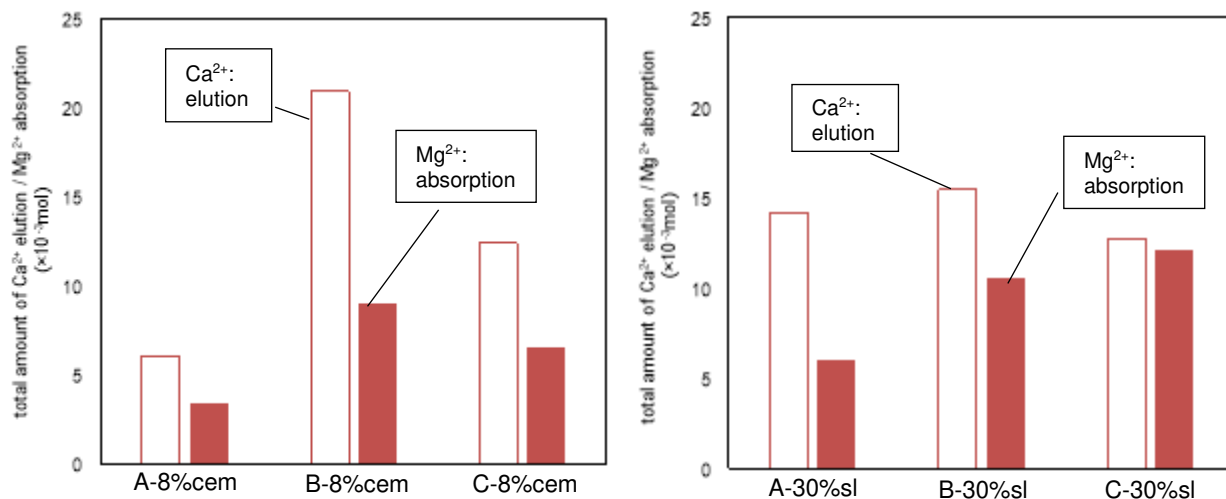*Figure 5. Ca^{2+} elution and Mg^{2+} absorption after 28 days exposure*

Figure 6. Ca^{2+} elution and Mg^{2+} absorption after 90 days exposure

5 CONCLUSION

In this study, we evaluated the long-term durability of slag-treated clay under seawater exposure by conducting unconfined compressive tests and measuring the calcium and magnesium ions. Our primary conclusions are summarized as follows. Slag-treated clay was more durable in seawater than the cement-treated clay.

The long-term durability under seawater exposure may be related to the clay's chemical components, e.g., silica, calcium, and aluminum. When exposed at 30℃, the degradation characteristics can be estimated by measuring the strength of the specimens exposed for 28 days. The ion exchange trend with the slag-treated clay differed from that of the cement-treated clay, which indicates that each binder involves a unique different deterioration mechanism.

However, additional information about the durability characteristics is required to promote the use of slag-treated clay. In addition, additional exposure tests with samples cured at higher temperatures will be necessary to estimate the durability of slag-treated clay. Thus, in future, we plan to identify the crystal structure formed in specimens to reveal the deterioration mechanism in more detail
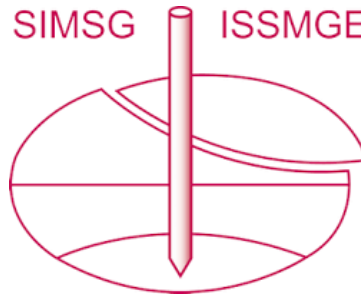
6 ACKNOWLEDGEMENTS

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