proceedings

International Seminar on
Architecture
in Urbanized Maritime Culture:

Chances and Challenges in
Planning and Design
for Sustainable Future

Hasanuddin University, Makassar - Indonesia
September 6th - 7th, 2013

50 years

Department of **Architecture**

1963-2013

**Proceedings of International Seminar on
Architecture in Urbanized Maritime Culture:
Chances and Challenges in Planning and Design for Sustainable Future**

**© Makassar, JurusanArsitektur
Fakultas Teknik Universitas Hasanuddin, 2013
III+1011 Hal. 21x29.7cm**

**Editor
Isfa Sastrawati
Venny Veronica Natalia
Widiasari Maruddani
Pratiwi Mushar
SyahrianaSyam**

**Jurusan Arsitektur
Fakultas Teknik Universitas Hasanuddin
Kampus Tamalanrea Jl. Perintis Kemerdekaan Km.10
Makassar 90245
Ph. 0411586265, Fax.0411587707**

Concrete Using Seawater as Mixing Water

Erniati¹⁾*, M. Wihardi Tjaronge²⁾, Rudy Djamaluddin³⁾, Victor Sampebulu⁴⁾

¹⁾ Doctoral Program, Civil Engineering, Hasanuddin University, e-mail: erni_nurzaman@yahoo.com

²⁾ Professor, Department Civil Engineering, Hasanuddin University, e-mail: tjaronge@yahoo.co.jp

³⁾ Associate Professor, Department Civil Engineering, Hasanuddin University, rudy0011@yahoo.com

⁴⁾ Associate Professor, Dep. Architecture Engineering, Hasanuddin University, e-mail: vicsam_ars@yahoo.com

Abstract

Seawater is one of natural resources that is very abundant. According to the United Nations in 2050, more than half of the world's population will not be able to get enough drinking water. Indonesia is an archipelago country so much that the quality of the source water area does not qualify as a drinking water. Concrete construction in areas that are likely very minimal quantity of fresh water or no, then the seawater cannot be avoided in mixing concrete.

This article is a review of the literature/prior research related to concrete using seawater. Mixing concrete using seawater on concrete can increase the compressive strength when compared to using fresh water. This is because the seawater does not interfere with the hydration process of the formation of calcium silicate hydrate gel/ tobermorite (CSH) and calcium hydrate/portlandite (CH). In addition to the salt content in the seawater that NaCl will react on fresh concrete will form salt crystals Friedel (Friedel's salt: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) which can improve the higher pH, and alkalinity increases so will activate the hydration of cement and provide structure pasta is more dense with pores smaller [15]. Otsuki et al [12,13], safe to use seawater as mixing water in the concrete. Thus, the possibility of seawater will be used as mixing water in concrete without reducing the strength and durability of concrete.

Keywords: (seawater, microstructure, concrete, friedel's salt)

I. Introduction

Concrete is a mixture of the constituent material consisting of cement, coarse aggregate, fine aggregate and water with or without additional ingredients. Qualified concrete is if the concrete has mechanical characteristics and good resistance. The most important mechanical characteristic of the concrete is compressing strength. This characteristic is related to the other properties, likewise the higher the compressing strength, the better the other properties are. One of the building blocks elements of the concrete is water that triggers the chemical process of cement as an adhesive /binder lubricates of the aggregate and to grease it to be easily done. Though generally the water used in the manufacture of concrete is potable /fresh water. Quantity and quality of water will affect the strength and durability.

In 2000, the world population was 6.2 billion. The UN estimates that by 2050, the world will get additional population of 3.5 billion with the biggest growth in developing countries which have experienced water crises [20]. The technical committee of JCI will state in 2050, according to the UN, more than half of the world's population will not be able to get enough drinking water, therefore saving serious fresh water is needed so that the use of seawater, the percentage is 97% of the total water on earth, is absolutely necessary. Increasing infrastructure development is in line with the needs of clean water more and more. In the concrete industry, several billion tons of water used in mixing the earth as water, water treatment (curing) and cleaner water every year, while the use of seawater is hindered [5].

Indonesia is an archipelago country where so many source water areas are not qualified as drinking water. Concrete construction in areas that are the quantity of water /fresh is possibly a

little or even nothing, thus the seawater cannot be avoided in concrete mixing and maintenance. According to Otsuki, et al [12, 13], in the near future water will be very difficult to obtain and is

International Seminar on Architecture in Urbanized Maritime Culture: Chances and Challenges in Design and Planning for Sustainable Future, and the 3rd CONVEESH, Department of Architecture, Faculty of Engineering, Hasanuddin University, Makassar, September 6-7, 2013

limited. Furthermore it is revealed that currently there are some areas where seawater or sand containing of chloride is used as water/ material mixing with or without intention.

In this life cycle, the civil engineering aspect, especially in the developed world has been thinking about the next challenge will be the less amount of the potential for clean water (fresh water) that can be used as mixing concrete. If the use of seawater on the development of infrastructure and industrial concrete is permitted, fresh water will be much more saved.

Seawater containing NaCl effects on concrete as Pruckner, F. and Gjørsv, O.E. [15] cited. The addition of sodium chloride in the fresh concrete will form salt crystals Friedel (Friedel's salt: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) can improve the higher pH, then the alkalinity increases so that it will activate the hydration of cement and provide pasta structure to become denser with smaller pores. Otsuki, N., et al [12,13], it is safe to use seawater as mixing water in the concrete as well as seawater had little effect on the strength and corrosion. Kaushik, S.K. and Islam, S [6], Falah M. W [2] have examined the concrete using seawater as mixing water and curing, with the result not so much difference with the concrete mixed with fresh or seawater. Kumar, S [7], the mixture of fly ash in cement concrete has increased resistance against seawater attack and the type of Ordinary Cement Pozolan modified by the suitable addition of it for the construction of sea structures. Aburawy, MM and Swamy, RN [1], the presence of chloride accelerates the development of early age strength of concrete with slag until about 7-14 days. After this age, there is a distinct disadvantage on the strength of concrete with chloride but the reduction of the strength is not significant. According to Shetty [17], seawater or water quality is not a factor that affects corrosion in concrete but the thing which affects corrosion is the permeability factor of the concrete and the lack of concrete cover.

II. The Cement Hydration Process

Cement hydration is the reaction between cement and water particles, including chemical and physical processes. The characteristics of fresh concrete, such as setting and hardening, is a direct result of hydration. Hard concrete characteristics are also influenced by the hydration process. Therefore, to understand the nature and behavior of cement and concrete, some knowledge of chemistry hydration is required. Portland cement hydration cement involves elements of reactions such as anhydrous calcium silicate and aluminates with water to form hydrated phases. Cement hydration is really complex so that the reaction of each element in the form of silicate cement (C_3S and C_2S) and aluminates (C_3A and C_4AF) is analyzed each singly.

II.1 The Hydrations of Silicates

Both C_3S and C_2S silicates react with water to produce amorphous silicate calcium hydrate known as CSH gel (Tobermorite gel) which becomes the main glue that binds particles of sand and aggregate together in concrete. C_3S is much more reactive than C_2S and in the standard temperature conditions, around 20°C ; about half of C_3S in cement will be hydrated in 3 days and 80% within 28 days. In contrast, the hydration of C_2S usually lasts up to 14 days normally. The excess of Ca is precipitated as crystals of hydroxide calcium, $\text{Ca}(\text{OH})_2$ or portlandite (CH). C_2S hydration also produces several formations of CH.

$\text{Ca}(\text{OH})_2$ liberated by silicate calcium hydrolysis to form thin hexagonal plates, with tens of micrometer distance among the plates, but then it is joined into a large deposit. Hydration reaction can be seen in Equation 1 and 2.

Or by using the stoichiometric equation can also be simplified as in Equation 3 and 4 [11, 21].

II.1.1 The Hydration of Aluminate

Aluminate phase composition in clinker and the cement hydration is strongly influenced by the large quantity of silicate reaction and by the presence of a base as well. In the absence of a solution of calcium sulfate, C₃A reacts quickly to form C₂AH₈ and C₄AH₁₉ phase, which then converts to C₃AH₆. As seen in Equation 5, 6 and 7 [21].

This reaction is highly exothermic and fast (flash set) and cannot be controlled kinetically. To control the C₃A hydration to prevent flash set, then during the manufacture of clinker it is added with gypsum.

If the ground gypsum has been pounded finely (CaSO₄·2H₂O) or in the form of hemihydrate (CaSO₄·0.5H₂O) mixed with C₃A before mixing it with water so the initial reaction can be controlled by ettringite (C₆A $\hat{S}$ ₃H₃₂), a protective layer formed on the surface of C₃A crystals. The reaction can be summarized as follows:

In which $\hat{S}$ is SO₃ and H shows H₂O.

Ettringite is usually called as Aft-phase. When available sulfate has been run out, ettringite reacts with C₃A to form a phase with a low content of SO₃ known as monosulfoaluminate. The reaction can be summarized as in Equation 10.

And along with the CH of C₃S and C₂S hydration reaction occurs as in Equation 11

Figure 1. Paste hydration products (left [14], right [9])

II.2 The Content Of Seawater

Romps, R.M. et al. [16], the existing water in the ocean is not formed as pure water associated with some salt, the experts agreed that the measurement of dissolved salt in seawater uses a unit of salinity. Seawater salinity generally ranges between 33-37 ‰ depending on the condition of the area, which has a lot of rainfall, river estuaries, ice and snow runoff and semi-enclosed areas. Especially, in the red sea often occurs very fast evaporation, salinity levels can reach 40 ‰. The main content of seawater is dominated by chlorine which reaches 55% of total dissolved salt, and then the second most abundant is sodium which reaches 30.61%.

Romps, R.M. et al [16], the water of the sea is the largest area that inhabits our planet, reaching 70.8%. Wikipedia [19], the seawater is a mixture of 96.5% pure water and 3.5% other materials such as salts, dissolved gases, organic matters and insoluble particles. Seawater

consisting of salinity of salt on average is about 35,000 ppm (3.5% or 35 g/ liter). The main chemical constituent of seawater is chloride (Cl), sodium (Na), magnesium (Mg), and sulfate (SO₄). Seawater pH values varied between 7.5 to 8.4. The surface seawater density ranges between 1.020

- 1.029. Of all the existing sources of water, salt water from the sea is the water with the highest amount reaches about 97% of the total amount of water that is in the earth, while the total amount of fresh water for is only about 3%. Where 2% of fresh water that is available in the form of ice in glaciers and the ice in north / south poles, whereas the remaining fresh water is 1% at most was in the ground and only a little in the surface of water.

II.3 The Influence Of Seawater In Concrete

In the hydration process of cement mixed with seawater will be affected by chemical bonding to form a new phase in the microstructure of concrete that affects the mechanical properties of concrete, especially on concrete durability. Chloride attack is the main cause of damage to concrete structures which are potentially forming mechanism of rust. When the chloride ions contained in the water reacts with the cement, the cement hydration products will mostly bind chloride ions in concrete either by binding chemically or through adsorption physically. The unbounded chloride ions by the hydration products will spread through the concrete pores and penetrated into the layers of galvanized steel [8].

Aburawy, MM and Swamy, RN [1], the presence of chloride accelerates the development of early age strength of concrete with slag until about 7-14 days. After this age, there is a distinct disadvantage on the strength of concrete with chloride but the strength reduction was not significant. Pruckner, F. and Gjorv, O.E. [15], the addition of sodium chloride natrium in the fresh concrete will form salt crystals Friedel (Friedel's salt: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) which can improve the higher pH, and alkalinity increases so that it will activate the cement hydration and provide more dense paste structure with smaller pores.

The most important parameter affecting the chloride binding capacity is the composition of the cement. C_3A quantity will determine the amount of the AFM phase, while the amount of C_3S and C_2S can be attributed into the amount of CSH obtained on hydration [8].

The main hydrate of cement paste is tobermorite (CSH gel), portlandite $\text{Ca}(\text{OH})_2$, ettringite / AFt ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), and AFm ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$). From hydrate, AFT and $\text{Ca}(\text{OH})_2$ has a small capacity to bind chloride, CSH has a very large surface and able to bind a variety of ions, including chloride ions. Furthermore, chloride binding capacity of CSH depends on the chemical composition and the surface area and the type chloride solution also the experimental conditions [10].

Based on the two-phase hydrations can bind more chlorides (CSH and AFM), has two main chloride binding mechanisms is through adsorption physically and through chemical reactions. CSH phase is known to bind chloride through absorption, whereas AFM chloride binding through chemical reactions forming Friedel's salt.

Islam, M. M. et al [4], Islam, Mad's. et al [3], the process of chloride attack on concrete in which NaCl and McGill after reacting with $\text{Ca}(\text{OH})_2$, the cement hydration results of chloride calcium occurs chemical reactions forming Friedel salt which can be seen in equation 12, 13 and 14.

Calcium chloroaluminate (Friedel's salt)

In the marine environment, chloride penetration into concrete derived from seawater to form Friedel salt. Friedel salt occupies a large volume after crystallization in the pores of the concrete rather than the compound which it replaced.

Islam. Md. S. et al [3], stated that in the marine environment, chloride ions penetrate into the concrete not only from the sea breeze but also sea carrying salt ions devastating and provide passive steel corrosion initiation. On the other hand, the principle reason of sulfate attack damaged concrete is the formation of gypsum and complex compounds known as calcium sulfoaluminate

(ettringite). Both of these products occupy a larger volume after crystallization in the pores of concrete rather than its replacement compounds. Bogue found gypsum hydrate formation causes an increase in volume of 17.7%. Chloride attack processes on concrete described by the following

chemical reactions. Both NaCl and MgCl₂ after reacting with Ca(OH)₂ from cement hydration in the form of a soluble calcium chloride will be leached out and will cause material losses and impairment. MgSO₄ also reacts with Ca(OH)₂ and CaSO₄·2H₂O (Gypsum), which in turn reacts with aluminates hydrate calcium to form additional aluminates sulfate hydrate (ettringite).

The excess formation of soluble chloride calcium delivers results increasing permeability of the concrete causing material losses and weakening. Ettringite formation is associated with expansion and cracking. Therefore the adverse effects associated with the chemical reaction that manifests physical effects, such as changes in volume, weight, permeability and the other properties of concrete.

Otsuki, et al [12,13], it is safe to use seawater as mixing water in the concrete as well as seawater has little effect on the strength and corrosion. Kaushik, S. K. and Islam, S [6], Falah M. W. [2] having examined the concrete using seawater as mixing water and curing, with not so much different result with concrete mixed with fresh water or seawater. Tjaronge, MW [18], seawater does not interfere with the hydration process of hollow concrete experiencing of immersion in seawater. Kumar, S [7], the mixture of fly ash (10% and 20%) in cement concrete has increased resistance against seawater attack. The Ordinary Cement type is a potential option modified by the addition of suitable Pozolan for the construction of marine structures. Shetty [17], seawater or water quality is not a factor that affects corrosion in concrete but its factor is the permeability of the concrete and the lack of concrete cover.

Pruckner, F. and Gjørsv, O.E. [15], Portland cement generally provides excellent protection on all steel embedded in concrete both chemical and physical. Chemical protection is mainly provided by the high alkaline properties of water pore (pH 13.0 to 13.5), in which steel becomes the passive electrochemical. In addition, the physical protection is provided by the concrete by slowing or preventing the penetration of aggressive species such as chloride or carbon dioxide to the steel / interface concrete. The addition of sodium chloride in the fresh concrete will form Friedel's salt crystals (3CaO. Al₂O₃. CaCl₂. 10H₂O) which can improve the higher pH, and alkalinity increases so it will activate the hydration of cement and provide paste structure to be more dense with smaller pores.

III. CONCLUSIONS

Seawater used as mixing water does not interfere with the hydration process of concrete and increase the compressive strength on concrete. Besides, the concrete using seawater can increase higher pH and provide paste structure to be more denser with smaller pores. This possibility occurs due to the presence of formed salt crystals called Friedel. Hydration products of concrete using seawater are such as CSH, CH, Friedel salt and ettringite. The possibility of seawater can be used as mixing water on concrete.

REFERENCES

- [1] Aburawy, M.M. and R. N. Swamy (2008). *Influence of salt weathering on the properties of concrete*, The Arabian Journal for Science and Engineering, Vol. 33, Number 1B.
- [2] Falah, M. W. (2010). *Effect of seawater for mixing and curing on structural concrete*, The IES Journal Part A: Civil & Structural Engineering, Vol. 3, No. 4, 235-243.
- [3] Islam, Mad's, Kaushik, S.K., and Islam, Md.M. (2005). *Physical and mechanical behaviour of concrete In seawater under hydrostatic pressure*, Journal-The Institution of Engineers, Vol.66 No.2, Malaysia
- [4] Islam, M. M., Islam, M. S., Mondal, B. C., and Islam, M.R (2010). *Strength behavior of concrete using slag with*, Journal of Civil Engineering (IEB), 38 (2) 129-140

- [5] JCI-TC-121A, *Technical committee on the use of seawater in concrete*, <http://www.jci-net.or.jp/~tc121a/shushi-E.html/> accessed 17th Mei 2013.
- [6] Kaushik, S. K. and Islam, S (1995). *Suitability of seawater for mixing structural concrete exposed to a marine environment*, *Cement & Concrete Composites* 17 (1995): 177–185
- [7] Kumar, S (2000). *Influence of water quality on the strength of plain and blended cement concretes in marine environments*, *Cement and Concrete Research*, 30(3), 345–350.
- [8] Marinescu, M.V.A. & Brouwers, H.J.H (2010), *Free and bound chloride contents in cementitious materials*, 8th fib PhD Symposium in Kgs. Lyngby, Denmark.
- [9] Mehta, P.K and Monteiro, P.J.M (2005). *Concrete: Microstructure, properties and materials*, 3rd Ed, McGraw-hill Professional.
- [10] Mien, T.V., Nawa, T., Kurumisawa, K (2008). *Contributions of C-S-H and AFm hydrates to chloride binding isotherms of various cements*, The 3rdACF International Conference- ACF/VCA, 2008
- [11] Neville, A.M. and Brooks, J.J (2010), *Concrete technology*, Prentice Hall, 2nd Ed.
- [12] Otsuki, N., Furuya, D., Saito, T. And Tadokoro, Y (2011). *Possibility of seawater as mixing water in concrete*, 36th Conference on Our world in Concrete & Structures, Singapore.
- [13] Otsuki, N., Saito, T. and Tadokoro, Y (2012), *Possibility of seawater as mixing water in concrete*, *Journal of Civil Engineering and Architecture*, Vol 6, No. 10 pp. 1273–1279, USA
- [14] Chompreda, P (2010), *Construction Material: Concrete*, Mahidol University, Thailand
- [15] Pruckner, F. dan Gjörv, O.E (2003), *Effect of CaCl₂ and NaCl additions on concrete corrosivity*, *Cement and Concrete Research*, 34 (2004) 1209–1217.
- [16] Romps, R.M, Rumampuk, N.DC dan Romps, J.R (2009). *Oseanografi kimia*, PT. Walaw Bengkulen, Jakarta Timur.
- [17] Shetty, M.S (1982). *Concrete technology teori and practice*, chap4, Chand & Company, New Delhi.
- [18] Tjaronge, M. W. 2012, *Teknologi Bahan Lanjut Semen dan Beton Berongga*, Telaga Zamzam, Makassar
- [19] Wikipedia (2013). *Seawater*, <http://en.wikipedia.org/wiki/Seawater>, accessed on Mei 26th 2013
- [20] Wikipedia (2013). *Sumber daya air*, <https://id.wikipedia.org>, accessed on Juni 2013.
- [21] Zongjin Li (2011). *Advanced concrete technology*, John Wiley & Sons, Inc, Canada.