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# STUDY OF CHEMICAL CONCENTRATION OF MAIN INGREDIENTS FOR MAKING PORTLAND COMPOSITE CEMENT

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#### ABSTRAK

Penelitian ini bertujuan menentukan konsentrasi senyawa bahan baku utama pembuatan semen sebelum menambahkan aditif batu kapur dan menentukan kekuatan tekan serta porositas dan daya serap air dari semen sebelum menambahkan aditif batu kapur. Hasil penelitian menunjukkan bahwa semen dengan konsentrasi senyawa 3CaO.SiO<sub>2</sub> = 96,9%; 2CaO.SiO<sub>2</sub> = tidak ditemukan; 3CaO.Al<sub>2</sub>O<sub>3</sub> = 4,4%; 4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub> = 9,7%. Jika ditambahkan bahan aditif batu kapur maka akan menurunkan daya rekat dan menciptakan pori yang sangat luas sehingga dapat membuat suatu bangunan menjadi rapuh. Semen dengan konsentrasi seperti ini pun tidak dapat tahan terhadap reaksi unsur lain dari udara.

#### ABSTRACT.

This study aims to determine the concentration of the main raw material compounds of cement making before adding limestone additives and determining the compressive strength and porosity and water absorption of cement before adding limestone additives. The result showed that cement with concentration of  $3CaO.SiO_2 = 96.9\%$ ;  $2CaO.SiO_2 = negative$ ;  $3CaO.Al_2O_3 = 4.4\%$ ;  $4CaO.Al_2O_3.Fe_2O_3 = 9.7\%$ . If added limestone additive then it will decrease the adhesiveness and create a very wide pore can make a building becomes fragile. Such concentrated cement can not withstand the reaction of other particle from the air.

**Keywords:** raw material of cement, analysis of concentration of cement compound

#### I. Introduction

A trapezoid-shaped building with a thickness of 25 cm was found around the year 6500 BC in Yugoslavia, which is the beginning of the introduction of cement. Subsequently, Subsequently, in 1756 John Smeaton made mortar from a mixture of lime and clay that was burned, however in 1824, Joseph Aspdin from England filed a patent for cement produced by the combustion process from mixing limestone and clay (Botahala & Pasae, 2020). Cement is an adhesive material that is specially made from a mixture of limestone, clay, iron sand, with the help of gypsum which can harden when combined with water (Botahala, 2013).

In general, the cement manufacturing process according to (Botahala & Pasae, 2020) is as follows. Raw materials in the form of limestone and clay are transported to the crushing site to be broken and then transported to the material reservoir. From the reservoir, the material (limestone, clay, iron sand, silica

sand) is transported to the material comparison place for comparison arrangement, then it is transported to the mill to be milled as well as dried. From the mill, the material is transported and fed to the homogenization place. The complete homogenization results will automatically go to the combustion feed reservoir, while those that are not yet complete will be returned to be homogenized again. From the combustion feed collection place, the material is transported to the coagulation place for making lumps/granules before being burned in the furnace. Then the results of the combustion (clinker) are transported to the storage area to be cooled, and together with gypsum and other additives with a certain ratio are transported to the final mill to be ground into cement. After that, the cement is transported to the cement storage facility and then transported to the cement packing place. Once bagged, cement is ready to be marketed.

ASTM C-150-2004 data in (Botahala & Pasae, 2020), (Riyadi & Amalia, 2005), (van

Oss, 2005), and (Neville & Brooks, 2010) that the classification of Portland Cement is divided into 5 types, namely Type I is the cement for general use, meaning that this type of cement can be used in all environmental conditions and all types of buildings so it does not require special requirements. This type of cement is limited to a concentration of 3CaO.Al<sub>2</sub>O<sub>3</sub> not exceeding 15%; Type II is a cement whose use requires an environment that is resistant to sulfates. This type of cement is limited to a concentration of 3CaO.Al<sub>2</sub>O<sub>3</sub> not exceeding 8%; Type III is the cement that is used in a building with high strength in the initial stage after binding with a concentration of 3CaO.SiO<sub>2</sub> and 3CaO.Al<sub>2</sub>O<sub>3</sub> higher than type I cement; Type IV is a cement whose use requires low heat hydration. This type of cement has a relatively high concentration of 2CaO.SiO<sub>2</sub> and 4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub> and a relatively low concentration of 3CaO.SiO2 and 3CaO.Al<sub>2</sub>O<sub>3</sub>; Type V is a cement whose use requires an environment that has a high resistance to sulfates with a very low concentration of 3CaO.Al<sub>2</sub>O<sub>3</sub>.

Due to the dominant use of cement for general conditions, cement factories produced type I more cement than other types of cement. Therefore, cement testing in this study focused on the requirements for type I cement.

In order to participate as global citizens to reduce the impact of global warming by reducing CO<sub>2</sub> gas emissions, the cement industry has switched to producing Portland composite cement by reducing the use of clinker which is replaced with alternative materials in final grinding (Partana et al., 2010). According to Anonymous 2004 in (Botahala, 2013), Portland Composite Cement is the result of mixing Portland Cement with one or more powdered inorganic materials, including blast furnace slag, pozzolan, silicate compounds, limestone, with a total content of 6 - 35% of the cement mass. According to Anonymous 2004 in (Riyadi & Amalia, 2005) and (Botahala, 2013), a material is classified as Pozolan based on ASTM C 618-78, namely  $SiO_2 + Al_2O_3 + Fe_2O_3$  at least 70%. According to (Priyo N.S. & Sofyan, 2012), data from the 1999 Cembureau reported that the total CO<sub>2</sub> gas emission in cement production was 830 kg/ton of cement, with details as in Table 1.

**Table 1.** Carbon dioxide gas emissions in the cement production process.

CO <sub>2</sub> results from the process	The number of emissions (kg/ton cement)
CaCO <sub>3</sub> calcination	450
Coal	280
Operational	100

According to (Botahala, 2013), cement quality testing is carried out in two ways, namely chemically and physically mechanically. Chemically using the X-RF (X-Ray Fluorescence) method (Botahala, 2020) and calculations based on Bogue's stoichiometry to determine the concentration of chemical components in cement as well as physical mechanics through compressive strength tests, water absorption tests, and porosity tests. The Bogue stoichiometric equation (Botahala, 2013) and (Botahala & Pasae, 2020) explains that:

**First.** if A / F > 0.64 then:  $= (4,071 \times \%C) - (7,600 \times \%S) C_3S$  $(6,718 \times \%A) - (1,430 \times \%F)$  $-(2.852 \times \%S^{-})$  $C_2S$  $= (2,867 \times \%S) - (0,7544 \times \%C_3S)$  $= (2,650 \times \%A) - (1,692 \times \%F)$  $C_3A$ C<sub>4</sub>AF  $= (3,043 \times \%F)$ **Second,** if A / F < 0.64 then:  $= (4,071 \times \%C) - (7,600 \times \%S) C_3S$  $(4,479 \times \%A) - (2,859 \times \%F)$  $-(2.852 \times \%S^{-})$  $C_2S$  $= (2,867 \times \%S) - (0,7544 \times \%C_3S)$ = is not found in this cement.  $C_3A$ C<sub>4</sub>AF  $= (2,100 \times \% A) + (1,702 \times \% F).$ 

Limestone which is required in SNI-15-7064-2004 as an additive is the main raw material for cement production and this material is easily obtained in the vicinity of the cement factory so it does not require material procurement costs when compared to other additives (Botahala, 2013). However, based on the results of research (Marzuki, 2009) that each addition of 2% limestone as an additive to cement can reduce the quality of cement. This is also proven by (Botahala, 2013) that the Portland Composite Cement produced by P.T. Sarana Agra Gemilang KSO P.T. Kupang cement contains very high CaO (70.96%) so that when it reacts with water it will produce excess Ca(OH)2.

Clinker is formed from the process of burning raw furnace feed materials with a certain concentration of chemical components. ASTM C 150-2004 provides the main component concentration in the manufacture of type I cement as shown in Table 2 (Botahala & Manimoy, 2014).

**Table 2**. Concentration of Cement Chemical Components

<b>Cement Chemical Component</b>		Concen-
Name	Formula	tration (%)
Lime Oxide	CaO	63.23
Silica Oxide	$SiO_2$	20.17
Alumina Oxide	Al <sub>2</sub> O <sub>3</sub>	5.07
Iron Oxide	$Fe_2O_3$	2.66
Sulfur Oxide	SO <sub>3</sub>	3.26

The reaction of cement mineral formation, namely iron oxide reacts with alumina oxide and lime oxide to form compounds 4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub> otherwise known with the notation C<sub>4</sub>AF. The remaining alumina oxide reacts with lime oxide to form compounds 3CaO.Al<sub>2</sub>O<sub>3</sub> otherwise known with the notation C<sub>3</sub>A. lime oxide reacts with silica to form compounds 3CaO.SiO<sub>2</sub> otherwise known with the notation C<sub>3</sub>S and compounds 2CaO.SiO2 otherwise known with the notation C<sub>2</sub>S (Botahala & Pasae, 2020). ASTM C 150-2004 provides the formula for mineral concentration of Portland Cement Type I as shown in Table 3 (Tennis & Bhatty, 2006).

**Table 3.** Concentration of Cement Chemical Compounds

<b>Cement Chemical Compounds</b>		Concen-
Name	Formula	tration (%)
Alite	3CaO.SiO <sub>2</sub>	56.9
Belite	2CaO.SiO <sub>2</sub>	14.8
Celite	3CaO.Al <sub>2</sub> O <sub>3</sub>	8.9
Brownmillerite	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	8.2

In general, the concentration and mineral properties of Portland Cement are:  $3\text{CaO.SiO}_2$  (50-70)% which provides fast hydration and binding and contributes to initial strength,  $2\text{CaO.SiO}_2$  (10-30)% which provides slow hydration and strength. in the long term,  $3\text{CaO.Al}_2\text{O}_3$  (3-13)% which provides very fast hydration, high hydration heat, contributes to binding and initial strength, and  $4\text{CaO.Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$  (5-15)% which provides fast hydration properties, and cement color (Botahala & Pasae, 2020).

### II. Materials and Methods

#### 2.1. Research Materials and Tools

Materials to be used in this research consist of limestone, clay, and silica sand, from PT. Sarana Agra Gemilang KSO PT. Semen Kupang and water.

The tools used in this study consisted of measuring cups (500 ml capacity), digital scales (2000 gram capacity), basins, buckets, ovens, plastic bags, sieve no. 230 (230 mesh) = 0.063 mm (63  $\mu$ m), blender, slag furnace, standard mixer machine, stirrer, and mixing bowl, cube-shaped specimen mold with sides 5 cm, compactor, leveling spoon, steel ruler with length 20 cm, and a press machine (ELE International), X-RF (Thermo Scientific), and a stopwatch.

#### 2.2. Method / Procedure

Raw materials that have been refined are taken according to the proportions

applicable at PT. Sarana Agra Gemilang KSO PT. Semen Kupang, namely 76% limestone, 16% clay, 1.60% iron sand, and 6.40% silica sand. The raw materials are then mixed and burned in a furnace with a temperature of 800 °C for 8 hours until slag or clinker is formed. The clinker is then mixed with gypsum according to the provisions of PT. Sarana Agra Gemilang KSO PT. Semen Kupang and mashed in a blender and sieved with a sieve number 230. The result is the cement that is ready for testing.

#### III. Results and Discussion

The results of the characterization of X-RF on cement without additives as raw material for making portland composite cement are as shown in Table 4.

**Table 4**. Concentration of Cement Chemical Components

<b>Cement Chemical Component</b>		Concen-
Name	Formula	tration (%)
Lime Oxide	CaO	68.20
Silica Oxide	SiO <sub>2</sub>	19.18
Alumina Oxide	$Al_2O_3$	3.70
Iron Oxide	Fe <sub>2</sub> O <sub>3</sub>	3.18
Sulfur Oxide	$SO_3$	2.11

These results when compared with ASTM C 150-2004 in Table 2, show that the concentrations of CaO and  $Fe_2O_3$  are higher while the concentrations of  $SiO_2$ ,  $Al_2O_3$ , and  $SO_3$  are lower, as seen in Figure 1.

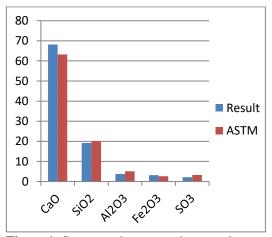


Figure 1. Concentration comparison graph cement chemical components

Thus, the selection of additives in the manufacture of Portland composite cement must be done selectively. The selected additives preferably contain pozzolanic ingredients ( $SiO_2 + Al_2O_3 + Fe_2O_3$ ) higher than 75% (Botahala, 2013).

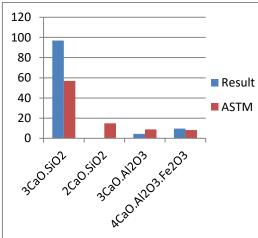
Bogue's Stoichiometry calculations on the characterization results of X-RF which have been presented in Table 4, were carried out using the first Bogue equation, considering that the  $Al_2O_3$  /  $Fe_2O_3$  comparison value exceeds 64%. The calculation results can be seen in Table 5.

**Table 5**. Concentration of Cement Chemical Compounds

Cement Chemical Compounds		Concen-
Name	Formula	tration (%)
Alite	3CaO.SiO <sub>2</sub>	96.9
Belite	2CaO.SiO <sub>2</sub>	Not found
Celite	3CaO.Al <sub>2</sub> O <sub>3</sub>	4.4
Brownmillerite	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	9.7

These results indicate that this raw material lacks one of the components of the pozzolanic material, namely SiO<sub>2</sub>, and has a high CaO component. So that when the homogenization process occurs, the chemical components of this cement can only form brownmillerite and celite, the rest, with very minimal concentrations, react with CaO to form alite.

The results of the calculation of the concentration of cement chemical compounds as in Table 5, when compared with ASTM C 150-2004 in Table 3, can be used as raw material for making Portland composite cement by adding the right pozolanic additives. Furthermore, Figure 2 shows the comparison of the concentration of type I cement chemical compounds and the concentration of raw materials for making composite protland cement.



**Figure 2.** A graph of the comparison of the concentration of cement chemical compounds

These results indicate that the hydration process will become unstable because of the concentration of 2CaO.SiO<sub>2</sub> is not found. If limestone additives are added, the result will be a decrease in the concentration of other compounds which can affect the decrease in cement adhesion. While the 3CaO.SiO<sub>2</sub> concentration will automatically increase so

that it will produce excess Ca(OH)<sub>2</sub> which is strong alkaline after being hydrated due to high CaO minerals from limestone. So it is important to determine the right additives in the manufacture of composite Portland cement to obtain results according to type I cement standards.

#### IV. Conclusions

The results of the chemical analysis show that cement with a concentration of this compound if only 2% of limestone additives are added will reduce adhesion (Marzuki, 2009) and cause very large pores which can make buildings brittle. Even cement with this concentration cannot withstand the reactions of other substances from the air. So it is recommended to use additional material of husk ash (Botahala et al., 2013) because according to (Botahala, 2020) rice husk ash has a very high concentration of silica oxide.

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