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# Use of Chemical Additive for Production of Portland Cement Based Binder with Less CO<sub>2</sub>

Yohannes Lim<sup>1</sup>

<sup>1</sup>PT. Sika Indonesia, Indonesia Jl. Raya Cibinong-Bekasi Km.20, Limusnunggal - Cileungsi, Bogor - 16820, yohannes@id.sika.com

#### ABSTRACT

Portland cement based binder is major material used in the construction field market. Production of Portland cement involves two main processes, pyroprocessing and comminution. Both of these processes release  $CO_2$ . During the first process, pyroprocessing stage, main active material of Portland cement, clinker, is produced. Next process, through the comminution stage to form Portland cement, clinker is ground and blended together with other raw materials in order to obtain end product that will allow the hydration reaction with water. Use of chemical additive can result in less  $CO_2$  released to environment from the production of Portland cement based binder by the use of less clinker and energy used. Through the course of the current study, it is discussed, the working principle of chemical additive to allow less  $CO_2$  release to the environment as the result from the production of Portland cement based binder.

Keywords. Chemical, Additive, Production, Cement, CO<sub>2</sub>

### **INTRODUCTION**

Production of Portland cement (PC) based binder contributes ~5% of total CO<sub>2</sub> emitted to the environment globally (ICS, 2009). Because of this issue, cement producers are striving to reduce their CO<sub>2</sub> emission through more effective and efficient production processes. Production of PC based binder involves two main processes, both release CO<sub>2</sub>. These two processes are pyroprocessing and comminution. Estimated CO<sub>2</sub> released from pyroprocessing process is in the same amount to the clinker produced. Typical range of energy used for production of PC based binder is 100 – 120 kWh/ton and approximately 38% of this energy is used in comminution process (Alsop, et al., 2007). While coal based energy generator is used, it is equivalent to approximately 100,000 – 120,000 tonnes CO<sub>2</sub> per ton of PC based binder produced. Coal use releases ~0.093 kg of CO<sub>2</sub> to generate 1 kWh (Eggleston, et al., 2006). Decreasing CO<sub>2</sub> released from the production of PC based binder can be performed through several ways. One of them can be introduced during comminution process.

Decreasing  $CO_2$  during comminution process is performed by two approaches or mechanisms. First, by decreasing the portion of clinker per unit weight of PC based binder produced. Second, by decreasing the retention time of input materials in comminution process (less energy consumption per unit output of production). The use of these two approaches will alter the quality of end product (e.g. compressive strengths of hydrated end product will be decreasing). Use of chemical additive (cement additive) during comminution process allows the introduction of the two approaches to decrease  $CO_2$  while maintaining the quality of end product.

Cement additive has evolved significantly since its first invention. The first used of cement additive was back in 1930s with the main use to increase production rate. In 1970s, substances which found to enhance PC hydration (in addition to facilitate the increment in production rate) started to be used (Heller, et al., 2011). The common substances used for cement additive are glycols, alkanolamines and phenol-type compounds (Engelsen, 2008). Recently, advance development in polymer technology has delivered the use of polycarboxylate ether (PCE) as cement additive for its implementation in the comminution stage on the production process of PC based binder (Schrabback, 2009). Through several publications, the use of PCE based cement additive has been tested to have better performance in terms of grinding efficiency and property enhancer as compared to the known substances currently used as cement additive.



Figure 1. Typical cement additive application

Application of cement additive during comminution process is simple. In common application, it can be dripped into material just prior insertion to the grinding media. It can be applied into any common designed grinding media such as horizontal or vertical mill. Typical application can be seen in Figure 1. Another common application is dripping cement additive within the compartment of horizontal mill.

### WORKING PRINCIPLE OF CEMENT ADDITIVE

During comminution process of PC based binder production, unbalance charges at the surface of materials inside mill system creates three unwanted conditions. These are crack opening tend to close again, coating of milling media and the agglomeration of small materials which lead to less efficient of comminution process both in the grinding media and separator. Use of cement additive reduces the occurrence of these three unwanted conditions which results in increment of production capacity. The comparison on the conditions of the comminution process that is untreated and treated with cement additive is shown in Table 1.

Cement additive works by its complex surface interaction with PC based binder. This surface interaction happens within the process of comminution, which leads to the modification on surface behaviour of the particles of PC based binder. During mixing the system of PC based binder with water, interacted cement additive on the surface of PC based binder particle alters the chemical reaction of the system, which leads to better performance of the system before and after time of setting (compared to untreated system).

Table 1.	Comparison on condition during comminution process (untreated and
	treated with cement additive)

Condition o	Condition of comminution process untreated with cement additive							
Illustration			Fines					
Notes	<ul> <li>Cracks in particles which have started to develop close again.</li> </ul>	<ul> <li>Ground particles stick on grinding media softening the impact of grinding media.</li> </ul>	<ul> <li>Agglomerates of sufficiently ground particles are detected by the separator as coarse particles and consequently return to the mill for being further ground.</li> </ul>					
Condition o	f comminution process tre	eated with cement additive						
Illustration			Fines					
Notes	<ul> <li>Cement additive keeps the fracture surfaces stay separated, enabling easier crack formation to continue.</li> </ul>	<ul> <li>Cement additive reduces the coating effect and leads to intensified impact of the colliding balls.</li> </ul>	<ul> <li>Particles treated with cement additive are better dispersed when entering the separator.</li> </ul>					

# MATERIAL AND TESTING PROGRAM

Testing program in current study is designed to show the mechanism on how the implementation of cement additive facilitates the reduction of  $CO_2$  emitted during PC based binder production. Laboratory testing program was developed to closely follows the process of actual comminution process in plant. Actual comminution process of PC based binder involves four main processes. These are insertion of input materials (to be converted to end product), grinding, separation fine and coarse particles (by separator in closed comminution system) and quality control of end product. In laboratory program the input materials is OPC and fly ash, grinding process is using laboratory grinding mill and quality control of end product is using fineness and compressive strength tests.

Raw or input material and grinding time (energy needed to produce certain unit of end product) are the two factors influenced by the application of cement additive in order to decrease embedded  $CO_2$  of end product. Comparison of actual and developed simulating laboratory conditions (in terms of factors that influence embedded  $CO_2$  level of end product) is shown in Table 2.

Condition	Factors influencin	g CO <sub>2</sub>	Requirement of end
	Raw/input	Time related to	product related to milling
	material	grinding	process
Actual condition	Clinker,	Time needed to	Cement producer
	gypsum &	produce certain	specification (commonly:
	supplementary	amount of end	fineness and compressive
	material	product	strength)
Simulating	OPC and	Time to run	Fineness and
laboratory condition	fly ash	laboratory mill	Compressive strength

Table 2.	Comparison of actual and laboratory conditions in terms of factors
	influencing embedded CO <sub>2</sub> of end product

OPC and fly ash used for the simulation of input materials are commercially available in the market. The use of OPC is to provide the simulation on the input materials of clinker and gypsum. This OPC meets "ASTM C 150 type I Portland cement". Particles of the OPC resides on sieve#325 (opening size 45  $\mu$ m) is 8.7%. Fly ash is used as simulating material for the supplementary material. The fly ash has particles resides on sieve #325 of 7.6%. Strength activity index of fly ash (test following ASTM C 311"Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete") tested after 1, 3, 7 and 28 days are 88%, 96%, 94% and 94%, respectively.

In actual comminution process, raw materials are ground through specific length of time in order to obtain certain level of fineness. This certain level of targeted fineness is commonly used as the indicator of quality of end product especially compressive strength of hydrated end product. The quality control used as reference in current study is the values of fineness and compressive strength of the OPC ground for 5 minutes. Fineness is measured by ASTM C 430 "Standard Test Method for Fineness of Hydraulic Cement by the 45- $\mu$ m (No. 325) Sieve". Compressive strength test is performed following ASTM C 109 "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)".

Table 3 shows three approaches that can be used to decrease embedded  $CO_2$  during production (comminution stage) of PC based binder.

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Approach	Factor influencing lev	el of embedded CO2
Approach	Clinker factor	Energy (grinding time)
1	Constant	▼- reduced
2	▼ - reduced	Constant

▼ - reduced

▼ - reduced

3

 Table 3. Approach on decreasing embedded CO2 during production (comminution stage) of PC based binder

Table 4 shows the effect of cement additive and grinding time to the fineness of end product. Cement additive used in current study is SikaGrind<sup>®</sup> 871 ID (PCE based cement additive). Refer to its technical data sheet, SikaGrind<sup>®</sup> 871 ID is strength improver and grinding aid for being used in comminution process of PC based binder. Mix code used in current study is explained in Figure 2.

		G	5		F	2	2	SG	5	
Groun	d	Time of g minu	grinding, ates	Fly ash	Percentage of f (x 10 %)	'ly ash	SikaG	rind <sup>®</sup> 871 ID	Dosage of Sika (x 100 ppm	Grind 1)

Figure 2. Example of mix code

Table 4.	Effect of	chemical	additive and	grinding	time to fineness
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Approach	Mix code	OPC Fly Sika		SikaGrind	Grinding	Particles
			ash	871 ID,	time,	resides on
				$\mathrm{ppm}^\dagger$	minute	sieve #325
Reference	G5F0SG0	1	-	0	5	7.2
Approach	G4F0SG0	1	-	0	4	8.6
1	G4F0SG5	1	_	500	4	6.6
Approach	G5F20SG0	0.8	0.2	0	5	7.0
2	G5F20SG5	0.8	0.2	500	5	5.0
Approach	G4F20SG0	0.8	0.2	0	4	6.8
3	G4F20SG5	0.8	0.2	500	4	5.8

<sup>†</sup>Note: by weight of OPC or OPC + fly ash

After the input materials ground, they were mixed and tested for the compressive strength following ASTM C 109. Table 5 shows the result of compressive strength test result.

Approach	Mix code	Water :	ASTM	Compressive strength, MPa			MPa
		(OPC + fly)	C 1437	1 day 3 days		7 days	28 days
		ash)	flow				
Reference	G5F0SG0	0.485	114	13.24	22.00	25.86	40.68
Approach	G4F0SG0	0.485	119	11.63	20.49	25.28	40.96
1	G4F0SG5	0.485	123	15.75	24.70	32.21	48.57
Approach	G5F20SG0	0.442	114	10.40	19.18	23.82	36.56
2	G5F20SG5	0.431	108	13.80	23.45	30.45	46.14
Approach	G4F20SG0	0.442	113	10.01	18.65	26.99	39.03
3	G4F20SG5	0.432	106	14.22	23.27	27.68	46.99

Table 5. Effect of Chemical Additive to Compressive Strength

Figure 3 shows the effect on the use of cement additive and grinding time on the fineness of treated end product as compared to those untreated. Figure 4 shows the compressive strength after 1, 3, 7 and 28 days, respectively.



Figure 3. Comparison on fineness of end product



Figure 4. Compressive strength after 1, 3, 7 and 28 days

# ANALYSIS

Focus of the analysis is to demonstrate the mechanism on the application of cement additive for production of PC based binder with lower  $CO_2$ . The analysis is performed using the data obtained in current study and according to the three approaches as proposed in Table 3. The property of mix G5F0SG0 is used as the reference. Property (compressive strength) of the other mixes (untreated and treated with cement additive) is compared to that of reference mix. The result on the comparison is presented in Table 6.

Table 6.	Comparison on properties of treated and untreated mixes to reference
	mix

	Fac	tor	Illustration on the comparison of properties of treated and untreated mixes to reference mix
ach	leve embe	el of edded $O_2$	
Apprc	Clinker factor	Energy (grinding time)	Residue on sieve # 325 Compressive strength
1	Constant	Reduced	10 10 10 10 10 10 10 10 10 10
2	Reduced	Constant	10 10 10 10 10 10 10 10 10 10
3	Reduced	Reduced	<sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup> <sup>10</sup>

As it can be seen in Table 6, untreated mixes (G4F0SG0, G5F20SG0 and G4F20SG0) have lower compressive strengths as compared to the reference mix (G5F0SG0) except for the 28 days compressive strength of mix G4F0SG0. Drop on the compressive strengths are more pronounce in second and third approaches which involve the decrement of clinker factor. The use of cement additive provides the facilitation of higher compressive strength as can be compared between reference mix (G5F0SG0) and treated mixes (G4F0SG5, G5F20SG5 and G4F20SG5). It provides the evidence that the quality of end product (in current study compressive strength) can be maintained even though grinding time (retention time in actual comminution process) and clinker factor are lowered down to decrease embedded  $CO_2$  from the production of PC based binder.

Optimization on reduction of the level of clinker factor and grinding (retention) time is performed through industrial stage when the parameters of the mill are adjusted and the monitoring of quality of end product is performed.

In order to give the indication on the impact to the level of embedded  $CO_2$  through the implementation of the three proposed approaches, calculation of  $CO_2$  is performed by taking several assumptions. Assumptions taken are released CO<sub>2</sub> from energy used during clinker production is uncounted, released  $CO_2$  from the conversion of raw material into clinker is 525 kg/t (CSI, 2009) and released CO<sub>2</sub> from the energy used in grinding process is generated from coal. The other assumptions taken are that reference product is OPC (with 95% clinker and 5% gypsum), grinding time reduction is 20% and substituting material is 20% fly ash (with no embedded  $CO_2$ ). Typical energy used in grinding process is approximately 38% of total energy used to produces 1 ton of PC based binder, 110 - 120 kWh (Alsop, et al., 2007). It is used the value of 115 kWh for the calculation. The amount of  $CO_2$  released from the coal in order to generate 1 kWh is 0.093 kg (Eggleston, et al., 2006). The additional CO<sub>2</sub> embedded to the end product of PC based binder from the use of cement additive is ~0% per unit weight of cement. This assumption is based on the percentage of embedded  $CO_2$  per unit weight of cement additive produced is very low and the typical dosage of cement additive applied is only 200 – 1000 ppm by weight of PC based binder. The result of calculation is presented in Figure 5. More complex  $CO_2$  calculation with involvement of more detail parameters can follow the method provided by Cement Sustainability Initiative (CSI, 2009). It should be noted that values in the table in Figure 5 are the percentage of  $CO_2$  per unit weight of PC based binder produced. As an example, the production of 100 tonnes PC based binder through approach 3 will result in 40.23 (39.90 + 0.33) tonnes CO<sub>2</sub> and 10.06 tonnes less CO<sub>2</sub> as compared to the production of PC based binder untreated with cement additive (reference). The values in the graph are the percentage of total  $CO_2$  released from the production process without cement additive (e.g. the production of PC base binder through approach 3 released less 20%  $CO_2$  compared to production untreated with cement additive).



Figure 5. Comparison on the level of CO<sub>2</sub> reduced by the introduction of the three proposed approaches (as presented in Table 3 and Table 6)

### CONCLUSION

The application of cement additive allows  $CO_2$  reduction during production (comminution process) of PC based binder by two mechanisms. These are by allowing less energy used in production and less clinker used per unit weight of PC based binder produced while maintaining main interested property (e.g. compressive strength) achieved. Based on the analysis performed in current study, as shown in Figure 5, with all the assumptions used, the latter approach allows more significant  $CO_2$  reduction as compared to the first approach.

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