The cements used in concrete production biology essay

Business, Industries



Cement is a binder which chiefly consists of compounds of Ca, Si, aluminium, Fe and little sums of other stuffs. The cements used in concrete production are called hydraulic cements which set and harden after being combined with H2O.

In the earliest of the nineteenth century, Joseph Aspdin, a bricklayer, foremost made a hydraulic cement called Portland cement whose name was given since the hardened cement resembles the colour and quality of Portland rock [ErdoAYan T. S. , ErdoAYan Y.

T. (2007) , BaAYlayA±cA± Malzemelerin ve Betonun Onbin YA±llA±k Tarihi, ODTU YayA±ncA±lA±k.] . Portland cement is produced by closely blending together chalky and clayey, or other silica- , alumina- , and Fe oxide bearing stuffs, firing them in a kiln at a temperature about 1450A°C, and crunching the ensuing cinder with a little sum of gypsum (3-5 %) [Neville A. M. , Properties of Concrete, Fourth Edition, Pearson Education Limited, England, 2003] .

2, 1, 1,

Fabrication of Portland Cement Clinker

In order to bring forth Portland cement cinder, there are four basic elements which should be in the natural stuffs in an appropriate proportion. These natural stuffs are calcium oxide (CaO) , silica (SiO2) , aluminum oxide (Al2O3) and iron oxide (Fe2O3) . The beginnings of Ca oxide, which about constitutes the 65 % of the Portland cement cinder, are limestone, marl,

chalk and sea shells. The beginnings of silicon oxide are sand, clay and crushed rock.

The beginnings of aluminium oxide are shale, bauxite, clay and sand. The beginnings of Fe oxide are hematite, pyrite and clay. To bring forth high-quality cement, there is a certain bound for the natural stuffs and these typical altogether stuffs proportions are given in Table 2.

1. Table 2. 1 Typical natural stuffs proportions after inginition [O.

Labahn, Cement Engineers 'Handbook, Forth Edition, Bauverlag GmBH-Wiesbaden and Berlin, 1983.]

Oxide

Restricting Value (wt %)

Content (wt %)

CaO

60-69

65

SiO2

18-24

21

Al203

4-8

6

Fe2O3

1-8

3

MgO

& lt; 5, 0

2

K2O, Na2O

& lt; 2, 0

1

SO3

& lt; 3, 0

1

As given in Figure 2. 1, the crushed, land and screened homogeneous natural mix is fed into a rotary kiln at a temperature of 1250 – 1450A°C. The reactions take topographic point, during the Portland cement cinder production, are as follows: In the vaporization zone, as the name implies both the free H2O and the adsorbed H2O of the natural stuffs is evaporated between 100 and 400 oC. In the clay desiccation zone, between 350 and 650 oC, clay minerals decompose. At 550 oC, Ca carbonate starts to break up.

In the decarbonation zone, Ca carbonate quickly decomposes at 900 oC. In the combustion zone, with the decomposition of Ca carbonates formation of cinder minerals start. At 1200 oC, formation of dicalcium silicate (C2S), tricalcium aluminate (C3A) and tetracalcium aluminoferrite (C4AF) start. After the formation of these cinder minerals, tricalcium silicate (C3S) formation is achieved between 1250 and 1450 oC. Then, the end point cinder at a temperature 1450 oC is quickly cooled in order to avoid the sintering reactions to change by reversal.

The cooled cinder is ground with about 3-5 % gypsum to a specified grade of choiceness. The ground behind the gypsum add-on is to set the scene clip of the cement. Finally, the ensuing merchandise is commercial Portland cement so widely used throughout the universe [O.

Labahn, Cement Engineers 'Handbook, Forth Edition, Bauverlag GmBH-Wiesbaden and Berlin, 1983 / Ramachandran V. S., Concrete Admixtures Handbook, Second Edition, Noyes Publications, United States of America, 1995].

Admixtures

Cement Silo

Fuel Preparation

Prey

Raw Crunching

Homo Silo

Gypsum + Additive

Crusher

Raw stuff

Cooling

Finish Crunching

Preheater

Kiln

Filter

Stack

Cinder

Figure 2. 1 Flow sheet of Cement Production

2. 1. 2.

Chemical Composition of Portland cement

In cement, there are basically four cinder stages which are listed in Table 2.

2. Determination of these stages of cement is a really complex process.

However, estimates for the cinder phases 'composing for Portland cement

can be achieved with its oxide analysis (see Table 2. 1.) by utilizing Bogue ' s expression. Table 2.

1 Cement Clinker Phases. [Cements, Graeme Moir]

Appellation of the stage

Composition of the pure stage

Abbreviated Notation

Typical scope

(mass %)

Alite or Tricalcium silicate

3CaO. SiO2C3S45-65

Belite or Dicalcium silicate

2CaO. SiO2C2S10-30

Aluminate or Tricalcium Aluminate

3CaO. Al2O3C3A5-12

Ferrite or Calcium Aluminoferrite

4CaO. Al2O3. Fe2O3C4AF6-12C3S = 4.071 (entire CaO - free calcium hydroxide) - 7.

600SIO2 - 6.718A1203 - 1.430Fe203 (2.1)C2S = 2.867SIO2 - 0.7544C3S (2.2)C3 A = 2.65A1203 - 1.

692Fe203 (2.3)C4AF = 3.043Fe203 (2.4)

Hydration of Phases in Portland cement

The series of reactions take topographic point during the hydration of cement with H2O which consequences puting and indurating of concrete.

As stated in [Handbook of thermic analysis of building stuffs Vangipuram Seshachar Ramachandran] , the rate of hydration of cement depends on the crystal size, imperfectnesss, atom size, atom size distribution, the rate of chilling the cement cinder, surface country, the presence of alloies, the temperature etc. which consequences a complex hydration procedure. Due to the complexness of cement hydration, it is appropriate to analyze the reactions of cinder stages individually. C-S-H gel which is the chief binding stuff which binds the sand and aggregative atoms together in concrete is formed by reaction of both C35 and C25 with H2O. The reactions are summarized in Equation (2. 5) and (2. 6) . C3S is much more reactive than C2S under normal temperature conditions.

Therefore, C3S contributes more to early strengths. However, the hydration of C2S is much slower. 2C3S + 6H a†' C3S2H3 + 3CH (2. 5)Tricalcium Water C-S-H Gel CalciumSilicate Hydroxide2C2S + 4H a†' C3S2H3 + CH (2) (2. 6)Dicalcium Water C-S-H Gel CalciumSilicate HydroxideThe Ca silicate hydrate (C-S-H) gel, which is responsible for the cement paste strength, scene and hardening, occupies a high per centum age of the entire solids in a cement paste.

The other major constituents of Portland cement cinder, tricalcium aluminate and Ca aluminoferrite besides respond with H2O. Since these cinder minerals

besides react with gypsum, their hydration chemical science is more complicated. The hydration reaction of C3A with H2O given in Equation 2. 7 is really rapid, but C3A has non any part to strength of the cement. However, hydration of C3A has an inauspicious consequence on the lastingness of cement.

Therefore, gypsum is added to retard the hydration of C3A. C3A + 3CA H2 + 26H a†' C6AA 3H32 (2. 7)Tricalcium Gypsum Water

EttringiteAluminateAlthough the gypsum is consumed wholly if C3A still remains, another reaction given in Equation 2. 8 takes topographic point: 2C3A + C6AA 3H32 + 4H a†' 3C4AA H12 (2. 8)Tricalcium Ettringite Water Calcium AluminoAluminate Monosulfo HydrateThe hydration reaction of C4AF, which has a slower reaction rate compared to hydration of C3A, contributes less to strength of Portland cement. The reaction of C4AF with H2O is as follows: C4AF + 3CSH2 + 21H a†' C6 (A, F) S3H32 + (A, F) H3 (2. 9)Tetracalcium Gypsum Water Calcium (Iron, Aluminum)Aluminoferrite Trisulfo Aluminate HydroxideAlthough the gypsum is consumed wholly, if there is still C3A, so the following reaction occurs: C4AF + C6 (A, F) S 3H32 + 7H a†' 3C4 (A, F) SH12 + (A, F) H3 (6)Tetracalcium Calcium Water Calcium (Iron, Aluminium)Aluminoferrite Trisulfo Monosulfo HydroxideAluminate Aluminate

Main Components of Cement

The chief cementitious stuff in concrete is cement.

However, to diminish the cost, to better the concrete public presentation and to bring forth more environmental friendly merchandises several auxiliary cementitious stuffs, which are by and large natural minerals or byproducts of some other industrial procedures, are used in cement. Therefore, cement consists of different stuffs which are homogeneous in composing. The chief components of cement other than cinder listed in TS EN 197-1 are as follows: Pozollanic stuffsNatural Pozzolana (P)Artificial PozzolanaSilica smoke (D)Granulated Blast Furnace Slag (S)Fly Ash (V, W)Siliceous fly ash (V)Calcareous fly ash (W)Burnt shale (T)Limestone (L, LL)The per centums of these stuffs in cements vary from cement type to cement type and depending on the application and the belongingss of concrete desired. However, TS EN 197-1 provinces that the composing of the cements conform this standard shall be in the bounds given in Table 2. 3.

Table 2. 3 Cement Composition Percentages Harmonizing to TS EN 197-1.

Pozollanic stuffs

Although, pozzolanic stuffs do non indurate in themselves when assorted with H2O, they exhibit cementitious belongingss when combined with Ca hydrated oxide at normal ambient temperature.

Silisium dioxide (SiO2) and Aluminium oxide (Al2O3) are the major compounds in pozzolanas. The minor compounds in pozzolanas are iron oxides (Fe2O3) and others.

Natural Pozzolana (P, Q)

Materials originated from volcanic eruption are normally called as natural pozzolanas [Progresss in cement engineering: chemical science, industry and testing, S. N. Ghosh] . Harmonizing to TS EN 197-1, there are two types of natural pozzolana, viz.

natural and natural calcined pozzolanas denoted by P and Q, severally.

Artificial Pozzolana

Artificial pozzolans are the byproducts of assorted thermic interventions, such as burned shale, silicon oxide smoke, wing ash, scorias, etc.

Silica smoke (D)

Silica smoke, besides called condensed silicon oxide smoke and micro silicon oxide, is a finely divided residue ensuing from the production of elemental Si or ferrosilicon metals that is carried from the furnace by exhaust gases.

[Concrete Construction Engineering HandBook, Edward G. Nawy]

Granulated Blast Furnace Slag (S)

In the production of Fe, Fe ore is smelted in a blast furnace. During this procedure, run Fe that collects in the underside of the furnace and liquid Fe blast furnace scoria drifting on the pool of Fe, are sporadically tapped from the furnace at a temperature of 1400-1500a?°C.

[Lea 's chemical science of cement and concrete Peter C. Hewlett]
Granulated blast furnace scoria is made by rapid chilling of a scoria thaw
which contains at least two-thirds by mass of glassy scoria and has hydraulic

belongingss. TS EN 197-1 provinces that granulated blast furnace scoria composing shall has at least two-thirds by mass of the amount of Ca oxide (CaO), magnesium oxide (MgO) and silicon dioxide (SiO2). The remainder of the composing is Aluminium oxide (Al2O3) together with little sums of other compounds.

Besides, (CaO + MgO) / (SiO2) ratio by mass shall transcend 1, 0. [TS EN 197-1, Part 1: Composition, specifications and conformance standards for common cements, European Committee for standardisation, Brussels, 2000]

Fly Ash (V, W)

Fly ash is a finely divided residue that consequences from the burning of powdered coal and is carried from the burning chamber of the furnace by exhaust gases. Commercially available fly ash is a byproduct of thermic power workss. [Concrete Construction Engineering HandBook. Edward G.

Nawy]TS EN 197-1 divided fly ashes into two groups viz., silicious fly ash and chalky fly ash.

Siliceous fly ash (V)

Siliceous fly ash, a all right pulverization of largely spherical atoms holding Pozzolanic belongingss, consists chiefly of reactive Si dioxide (SiO2) and Aluminium oxide (Al2O3). [TS EN 197-1, Part 1: Composition, specifications and conformance standards for common cements, European Committee for standardisation, Brussels, 2000]

Calcareous fly ash (W)

Calcareous fly ash, a all right pulverization holding both hydraulic and/or Pozzolanic belongingss, consists chiefly of reactive Ca oxide (CaO) , reactive Si dioxide (SiO2) and aluminum oxide (Al2O3) .

[TS EN 197-1, Part 1: Composition, specifications and conformance standards for common cements, European Committee for standardisation, Brussels, 2000]

Burnt shale (T)

Burnt shale which is produced by combustion of oil shale in fluidized bed furnace between 600 and 800a?°C is another cementitious component used in cement production. Burnt shale is composed of cinder stages, chiefly dicalcium silicate and monocalcium aluminate.

Limestone (L, LL)

Limestone, a sedimentary stone, consists chiefly of Ca carbonate; the most stable signifier is calcite. Limestone frequently contains Mg, Al and Fe combined as carbonates and silicates. TS EN 197-1 provinces that to utilize limestone as a component in cement, Ca oxide content at least 75 % by mass.

Furthermore, limestone is divided into two groups in TS EN 197-1 harmonizing to its Total Organic Carbon (TOC) content. If TOC value does non transcend 0, 20 % by mass, the limestone is demonstrated with LL. If TOC value does non transcend 0, 50 % by mass, so the limestone is demonstrated with L.

Effectss of the Mineral Additives on Mortar and Concrete Properties

As mentioned before, minerals additives influences the belongingss of both cement and concrete. The undermentioned nowadayss the effects of chief component of cement on H2O demand, workability and strength.

Water Requirement

The sum of blending H2O required for a specified consistence of a howitzer or concrete is called as H2O demand of cement howitzer or concrete. Adding extra or less sum of H2O can take to inauspicious consequences on the strength of cement howitzer or concrete. Therefore, it is required to find how much H2O is sufficient for the cement howitzer or concrete.

Cementitious stuffs other than cinder have different impacts on the H2O demand of cement howitzer or concrete since they have different atom size, form etc. For illustration, Natural pozzolans have important consequence on H2O demand of concrete. Harmonizing to Vu et Al consequences, since the natural pozzolans increase the specific surface country, the H2O demand of cement incorporating natural pozzolans has higher H2O demand compared to ordinary Portland cement. Vu, D., Stroeven, P., and Bui, V. 2001.

"Strength and lastingness facets of calcined caolin-blended Portland cement howitzer and concrete." Cem. Concr. Compos., 23, 471-478.

The same consequence, addition in H2O demand, is besides observed when cinder is replaced with silica smoke in cement. However, for a given slack, H2O demand of a cement incorporating fly ash is less than the H2O demand

of a Portland cement. Although the dose of fly ash increases the H2O decrease additions, non all fly ash does the same consequence on howitzer. Harmonizing to Brink and Halstead findings (R. H. Brink and W. J.

Halstead, Studies associating to the testing of fly ash for usage in concrete, Proc. Am. Soc. Testing Mats. 56 (1956) (1956), pp.

1161-1206) as the C content of the fly ash increases the H2O demand additions.

Workability

Workability is defined as the relaxation of the concrete commixture, managing, packing, puting and completing. Water content of concrete has an of import consequence on workability. There are several factors impacting workability such as measure and features of cementing stuffs, and sum of H2O etc. Harmonizing to Pan et Al survey, the lubricant consequence and morphology betterment on cement howitzer or concrete of natural pozzolans addition with the addition in choiceness. As a consequence, natural pozzolans improve the consistence and the workability of the concrete.

[Influence of the choiceness of sewerage sludge ash on the howitzer belongingss Shih-Cheng Pana, Dyi-Hwa Tsenga, , , Chih-Chiang Leea and Chau Leeb]Li Yijin et al studied on use of fly ashes holding different choiceness as a cementitious stuff replacing the cinder in cement and replacing cement in concrete. They found out that fly ash improves the workability of cement howitzer or concrete due to their spherical form doing ball bearing " consequence. [Admixtures and Ground Slag for Concrete 1990]

; ACI Comm. 226 1987c The consequence of fly ash on the fluidness of cement paste, howitzer and concrete Li Yijin, Zhou Shiqiong, Yin Jian, and Gao Yingli]Besides, as Peter stated, the H2O demand of concrete incorporating land granulated blast furnace scoria decreases with the addition in the sum of land granulated blast furnace scoria. [Particular Concretes – Workability and Mixing Peter Bartos]Therefore, as the volume of all right atoms addition which taking to diminish in intervention of aggregative atom, for a given slack, fly ash, scoria and burned shale better the workability of concrete.

Strength

Supplementary cementitious stuffs such as fly ash, land granulated blast furnace scoria, burned shale and silicon oxide fume contribute to the strength addition of concrete. However, the features of the auxiliary stuffs and replacement degree limit them for the strength addition of concrete. For illustration, pozzolanic responsiveness of the fly ash is one of the modification parametric quantity [Fly ash in concrete: belongingss and public presentation edited by K. Wesche June 13th 1991] . In add-on to cementitious stuffs used, trial type is another factor impacting the strength. Because as the size of the specimen, wet content of the specimen, the rate of burden and type of trial machine alteration, the strength consequence alterations.

Factor Affecting Concrete Strength

Concrete is a composite stuff consisting of chiefly cement, H2O, coarse and all right sums and chemical alloies. Several complex reactions taking

topographic point when these stuffs are assorted consequence strength addition of the concrete. There are several factors impacting the strength of concrete. As mentioned above, since the concrete is a mixture of cement, H2O, coarse and all right sum and chemical alloies, belongingss of each of these stuffs have an influence on the strength of concrete. For illustration, as

Importance of Flow

Flow trial, which depends on particularly the H2O to cement ratio and on assorted facets of the cement such as choiceness, flocculation, and rate of hydration reactions, gives an thought about the consistence of a cement howitzer or a fresh concrete and it [Significance of trials and belongingss of concrete and concrete-making stuffs, Joseph F. Lamond, J. H. Pielert] .

Consistency is an of import parametric quantity for the concrete workability. In add-on, as Joseph F. Lamond and Pielert stated, by utilizing a standard consistence, i. e.

utilizing a criterion flow, mistakes because of consolidation or hemorrhage in samples will be avoided.

Inter-Laboratory Test Evaluation

An inter-laboratory trial is carried out by a representative figure of take parting research labs repeatedly within each take parting research lab on indistinguishable samples under in agreement conditions. There are three chief aims for inter-laboratory testing: Proficiency TestingCertification of MaterialsTest Method ValidationThe preciseness, which is a cardinal feature of a trial method, is the grade to which the perennial trials under the same

conditions show the same consequences. In this survey, since an interlaboratory trial is an appropriate process to mensurate the preciseness of a trial method, an inter-laboratory trial is applied to prove the preciseness of the trial method prescribed in TS EN 196-1.

Appraisal of Inter-Laboratory Test Consequences

In the inter-laboratory trial method carried out in this survey, the appraisal of the trial consequences is carried out in conformity with TS EN 196-1 and Normal Gauss Distribution.

Credence of Test Results

Credence of trial consequences was determined harmonizing to TS EN 196-1. For each mold, if there is any consequence demoing 10 % aberrance from the mean of the six consequences, so one of these consequences is cast-off. Then, the staying five consequences are averaged.

If once more, there is any consequence demoing 10 % aberrance from the mean of the five consequences, so all of the consequences are discarded.

Omission of Outliers

Since the undue minimisation of the utmost values consequences in an feeling of the public presentation of the trial method, the extreme values called outliers for each information set were omitted. To find the outliers of the remainder of the informations sets, Grubb 's Test was applied. Since the Grubb 's trial is valid for informations set which is usually distributed, normalcy of the remainder of the information was checked with a computing machine plan called SPSS. In SPSS, normalcy is checked by Kolmogorov-

Smirnov Test which serves as a goodness of fit trial to a normal distribution.

The hypotheses used in this trial are: Holmium: there is no difference between the distribution of the information set and a normal oneHour angle: there is a difference between the distribution of the information set and normalThe P-value is provided by SPSS, if it is below 0. 05, so the information set is non usually distributed. In Grubb 's Test, by ranking the information set, the smallest and the largest values are determined.

Then, the mean and the standard divergence are calculated. Depending on the intuition of a possible outlier of a value, one of the undermentioned equations is used [Basic statistics and pharmaceutical statistical applications, James E. De Muth]:

(2.5)

(2.6)

Then, the deliberate T values are compared with the critical value given in Table 2.

Table 2. 3 Critical Valuess for Grubb 's TrialNgcritI $\pm = 0.05$ gcritI $\pm = 0.01$

A

 $Ngcritl \pm = 0.$

 $05gcritl \pm = 0.01$

A

 $Ngcritl \pm = 0.05gcritl \pm = 0.0131.15311.1546$

A

152. 40902.

7049

A

803. 13193. 520841. 46251. 4925

A

162. 44332. 7470

A

903.

17333. 563251. 67141. 7489

A

172.

47482. 7854

A

1003. 20953. 600261. 82211. 9442

A

182.

50402. 8208

A

1203. 27063. 661971. 93812. 0973

A

192. 53122. 8535

A

1403.

32083. 712182. 03172. 2208

A

202. 55662. 8838

A

1603. 36333.

754292. 10962. 3231

A

252. 66293. 0086

A

1803.

40013. 7904102. 17612. 4097

A

302. 74513.

1029

A

2003. 43243. 8220112. 23392.

4843

A

402. 86753. 2395

A

3003. 55253. 9385122. 28502. 5494

A

502.

95703. 3366

A

4003. 63394. 0166132. 33052. 6070

A

603.

02693. 4111

A

5003. 69524. 0749142. 37172.

6585

A

703. 08393. 4710

A

6003. 74424. 1214

Evaluation of the Test Consequences

After happening out the outliers as described above, the rating of the trial consequences were performed. Since sample size was so little that the t-test was used to find the assurance interval. Harmonizing to the figure of informations sets which are included in the appraisal, t value matching to 95 % assurance for two-tail is chosen from t-tables given in Table 2.

3. Then, 95 % assurance interval is calculated with the equation given in 2. 8.

(2.

8)

Table 2. 4 t-TableThe Degreeof FreedomAccumulative ProbabilityFor two-tails0. 100. 050.

0250. 0116. 31412.

7131. 8263. 6622. 9204. 3036. 9659.

92532. 3533. 1824. 5415. 84142.

1322. 7763. 7474. 60452. 0152. 5713. 3654.

03261. 9432. 4473. 1433. 70771.

8952, 3652, 9983, 49981, 8602, 3062,

8963. 35591. 8332. 2622. 8213. 250101.

8122. 2282. 7643. 169111. 7962.

2012. 7183. 106121. 7822.

1792. 6813. 055131. 7712. 1602.

6503. 012141. 7612. 1452.

6242. 977151. 7532. 1312. 6022.

947In add-on to finding of assurance interval, computation of repeatability and the duplicability of the trial consequences are play an of import function upon an inter-laboratory trial rating. As Guslicov et Al mentioned, for 20 old ages, the advancement of the standard divergence of repeatability and duplicability and coefficient of discrepancy have given an thought on the advancement of the inter-laboratory trials. It is observed that during these periods, as the development of criterions and the reading and pertinence of the criterions addition, the coefficient of discrepancy lessenings.

Furthermore, Guslicov et Al concluded that there is an betterment in the participants 'studied on the trial method.

Besides, as stated in TS EN 196-1 and it can be seen on Figure 2. 4, for 28day strength, for the experient research labs under the conditions defined in TS EN 196-1, the repeatability in footings of coefficient of discrepancy is expected to be less than 6 % . Besides, it is besides stated in TS EN 196-1 that the repeatability in footings of coefficient of discrepancy is expected to be in between 1 % or 3 % . Figure 2. 4 Advancement of the coefficient of discrepancy for 1, 2 and 28-day compressive strength [Guslicov G, Coarna M, Pop A, Vlad C, Vlad N Accred Qual Assur (2009) 14: 541-546 Consideration refering interlaboratory trial for cement in the last 20 old ages]Therefore, for the obtained consequences, the standard divergence of repeatability and duplicability are calculated as given in equations 2. 9 and 2. 11, severally, which are defined in ISO 5725-2 [INTERNATIONAL STANDARD ISO 5725-211994] .

- (2.9)
- (2.10)
- (2.11)
- (2.12)

Where P denotes the entire figure of research labs take parting in the interlaboratory experiment, I denotes the figure of a peculiar research lab, J denotes the mold figure, n denotes the figure of trial consequences obtained in one research lab at one cast, denotes the arithmetic mean of the trial consequences, denotes the expansive mean of the trial consequences.

Comparison of the Test Results by Using Kruskal-Wallis Test Method

Kruskal-Wallis Test is a statistical trial method in which three or more informations sets can be compared whether informations samples belong to

the indistinguishable population or non. The hypotheses used in this trial are: Holmium: the samples are from indistinguishable populations. HA the samples are non from indistinguishable populations. The P-value, i. e. the Asymptotic Significance, is provided by SPSS. If it is below 0. 05, so the samples are non from the same population.