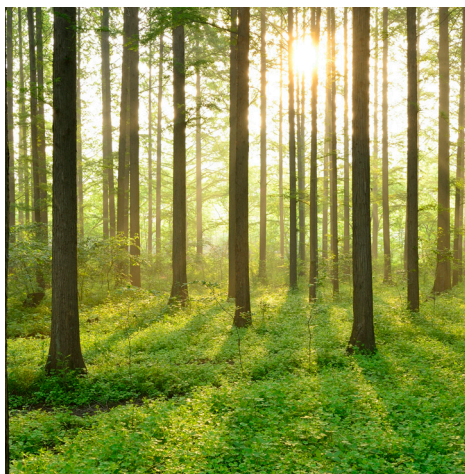


BOTTOM ASHES FOR GREEN AGGREGATE

REPORT 2021:795



Bottom ashes for green aggregate

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ISBN 978-91-7673-795-8 | © Energiforsk September 2021

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Foreword

Denna rapport är slutrapportering av projekt *2019-118 Bottenaskor för grön ballast* inom Askprogrammet som bedrivs av Energiforsk. Programmet verkar för att kunskap tas fram för att stimulera användningar av askor så att ingen eller ringa risk för hälsa och miljö på kort eller lång sikt föreligger.

Projektet har undersökt om slaggrus kan användas som ersättning för grus och sand i betong. Motivet är att hitta avsättning för bottenaskor från förbränningsanläggningar samtidigt som byggmaterialet blir lättare och ger ett lägre koldioxidavtryck.

Arbetet har genomförts av Chalmers tekniska högskola med Luping Tang som huvudprojektledare.

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These are the results and conclusions of a project, which is part of a research programme run by Energiforsk. The author/authors are responsible for the content.

Sammanfattning

Syftet med projektet har varit att undersöka om bottenaska från förbränningsanläggningar (MSWI) kan nyttjas för tillverkning av ballast med CO₂-gas som härdnings- och reaktionsmedium med målet att den konstgjorda ballasten kan användas i betongproduktion som ersättning för naturlig sand och sten.

Det genereras stora volymer bottenaskor från avfallsförbränning, som framför allt används för konstruktioner inom deponi. Efterfrågan för den typen av användning kommer minska i framtiden. Det finns i dagsläget ett stort behov av att utveckla tekniker som möjliggör ett säkert nyttjande av denna aska.

Å andra sidan är betong volymmässigt det mest använda byggmaterialet som består av cement och ballast, varav det förra har en hög koldioxidutsläpp i sin produktion medan det senare behöver konsumera naturresurser så som sand och sten, som blir mindre och mindre tillgängliga. Därför har tillverkningen av betong en stor klimatpåverkan genom användning av cement och ballast. Våra moderna utvecklade samhällen kräver en byggd miljö som är otänkbar utan den utbredda användningen av cementbaserad betong och hittills finns det inget annat alternativ som kan täcka behovet för en så stor efterfrågan. Därför är det ett faktum att vår civilisation har blivit starkt beroende av detta billiga men grundläggande byggmaterial - betong. Varje åtgärd som kan minska koldioxidavtrycket i betongproduktionen kommer säkert att bidra till FN:s globala mål för hållbar utveckling. Ett sätt för minskning av koldioxidavtrycket i betongproduktionen är att minska cementförbrukning genom att använda alternativa bindemedel som restprodukter från industriella processer, till exempel flygaska och masugnsslagg för delvis ersättning av portlandcement. Ett annat sätt är att använda återvunnen betong eller andra mineralmaterial som ersättning för ballast.

MSWI-aska innehåller betydande mängder kemiskt reaktiva och potentiellt hydrauliska kompositer bestående av oxider, dvs SiO₂, CaO och Al₂O₃, som kan användas som cementlösa bindemedel om de aktiveras ordentligt under lämpliga aktiveringsförhållanden. Å andra sidan kan dessa reaktiva kompositer, om de inte hydratiseras ordentligt, framkalla sprickor på grund av senare expansiva reaktioner i den hårdnade betongen. På grund av efterfrågan på hållbar avfallshantering är forskningsintresset för användningen av MSWI-aska i betong globalt stort, särskilt i de länder där utrymmet för deponering är begränsat. Tidigare forskningsinsatser inom detta område fokuserades på användningen av MSWI-aska för partiell ersättning av bindemedel och ballast. Det framgår av de publicerade artiklarna/rapporterna i litteraturen att användbarheten av MSWI-aska i betong fortfarande är begränsad till en liten mängd ersättning för portlandcement som bindemedel, ballast eller fyllmedel baserat på vissa empiriska försök. En av anledningarna till lågskaligt nyttjande av MSWI-aska som byggmaterial är det faktum att askan ofta innehåller en viss mängd metalliskt aluminium, vilket är skadligt om det används direkt i betong som ett viktigt konstruktionsmaterial som kräver långtidsbeständighet.

Detta projekt testar en ny idé som syftar till att undersöka om bottenaska kan användas för produktion av ballast med CO₂-gas som härdnings- och reaktionsmedium med målet att den tillverkade ballasten kan användas i betongproduktion som ersättning för naturlig sand och sten. Till skillnad från tidigare försök med enkel tillsats av aska i betong försöker vi med denna nya idé att först identifiera kemiska sammansättningar inklusive innehåll av skadliga ämnen och hydrauliska reaktiviteter i bottenaska med olika partikelstorlekar, och sedan använda de mindre skadliga delarna av bottenaska – delen med hydrauliska reaktiviteter som bindemedel och den relativt inerta delen som "frön" för tillverkning av stenkulor, som hårdas av CO₂-gas från t.ex. cementproduktionen. Under härdningen kommer CO₂ att reagera med kalcium för att bilda kalciumkarbonat. På detta sätt kommer metalliskt aluminium att reagera med den alkaliska lösningen i blandningen och helt enkelt införa luftporer i kulorna, medan kolsyran endast minskar kulornas alkalitet. När dessa kulor används i betong som ballast kommer inte defekterna inuti kulorna att påverka egenskaperna hos den nya cementbaserade matrisen i betong med avseende på motstånden mot kloridinträngning och armeringskorrosion. Därför bör denna nya idé leda till en lovande lösning för både återvinningsindustrin (mervärdesanvändning av bottenaska) och byggindustrin inklusive cementtillverkare (mervärdesanvändning av emitterad koldioxid) och betongtillverkare (minskande användning av naturliga sand och sten). Som en följd skulle detta då kunna bidra till att komma närmare målet om ett CO₂-neutralt klimat 2045.

Projektet omfattar tre arbetsdelar: 1) experimentell undersökning av kemiska sammansättningar och hydrauliska reaktiviteter, 2) produktion av grön ballast och 3) applicering av grön ballast i betong.

Bottenaskor, s.k. slaggrus med storlek 0-10 mm, som använts i detta projekt kom från två förbränningsanläggningar med en blandning av hushållsavfall och industriavfall. Askorna har lagrats i askackumulatorerna i flera månader före metallsortering. Därefter lagrades dessa metallsorterade askor i ungefär ett halvt år före leverans till Chalmers för undersökning i projektet.

Mättningsresultaten visar att askorna innehöll 14-15 % fukt. För att exkludera fuktinverkan som var utom projektskalen torkades bottenaskorna före olika provningar/undersökningar i projektet.

Arbetsdel 1: Baserat på askans kornfördelning delades varje aska upp i tre delar med kornstorlek 0-0,5 mm, 0,5-2 mm och 2-10 mm. Den kemiska sammansättningen i varje del av proverna analyserades och dess hydrauliska reaktivitet testades med en nyligen utvecklad metod. Av resultaten framgår det att två bottenaskor innehåller liknande kemisk sammansättning, dvs 13-20 % kisel, 12-17 % kalcium, 5,5-6,5 % aluminium och 4,4-5,9 % järn. Innehållet av tungmetaller i bottenaska från de två förbränningsanläggningarna varierar inte med kornstorleken, förutom kvicksilverhalt som är högre när kornstorleken är mindre. Resultaten från testning av hydrauliska reaktivitet visar att askorna blev hydratiserade troligen genom lagringen före/efter metallsorteringen.

Arbetsdel 2: Baserad på resultaten från arbetsdel 1 maldes slaggrus 0-10 mm till pulver med kornstorlek ≤ 0,25 mm för att släppa ut de latent

hydratiseringsegenskaper som kvarstår i de stora partiklarna under den tidigare härdningsprocessen och minska skadliga sprickor orsakade av deras långsamma kemireaktion i den hårdnade betongen vid senare ålder. En "två-steg" teknik har utvecklats för att tillverka stenkulor, dvs ballastmaterial, med mald bottenaska tillsammans med masugnsslagg under alkali-aktivering med vattenglas som alkali-aktivator. Det första steget är designat för utsläppning av skadlig vätgas ur det metalliska aluminium och dylikt som askan innehåller medan det andra steget är för tillverkning av stenkulor utan risken av sprickor orsakade av den skadliga gasen. Försök gjordes också för att förbättra den fina delen av återvunna betongballaster. Av resultaten framgår det att stenkulorna tillverkade av bottenaska och masugnsslagg har rimligt hög tryckhållfasthet, 5.6-6.4 MPa betydligt högre än dem (< 3 MPa) som rapporterades i litteraturen. De konstgjorda stenkulorna har en lägre densitet (ca 2300 kg/m^3) än natursten ($2650\text{-}2700 \text{ kg/m}^3$). Det innebär helt enkelt en mindre mängd material för en bestämd volym av betong, en lättare betongkonstruktion och en mindre transportbelastning. Efter förbättring blir den fina återvunna betongballastens kornstorlek större och bättre anpassad till den optimala ballastgraderingskurvan för betonggjutning.

Arbetsdel 3: De stenkulor som tillverkat av bottenaskor i arbetsdel 2 användes i en vanlig betong med hållfasthetsklass C35/45 för att ersätta natursten. Resultaten framgår att betongen med stenkulorna behövde mindre flytmedel för att nå samma konsistens. Det innebär att betongens bearbetbarhet/gjutbarhet har förbättrats av stenkulorna tack vare kulornas runda korn. Betongen med de konstgjorda stenkulorna visade också bättre motstånd mot kloridinträngning som är en viktig parameter för beständighet. Det är i stort sett på grund av stenkulornas hydratiseringsprodukter som har bra förmåga att binda kloridjoner som kloridinträngning förhindras. Å andra sidan minskade tryckhållfastheten hos betongen med stenkulorna på en viss nivå, men fortfarande uppfyllde den designade hållfasthetsklass. Det kan bero på grund av stenkulornas lägre densitet som leder till lägre elasticitetsmodul och som följd en mindre bärförmåga. Den förbättrade fina återvunna betongballasten (0-2 mm) tillsammans med den återvunna betongballasten (2-4 mm) användes i gjutning av en standard bruk enligt EN 196-1 för att fullt ersätta den naturliga sanden. Av resultaten framgår det att de fina återvunna betongballasterna kan fullt ersätta den naturliga sanden utan att försämra bearbetbarheten/gjutbarheten och tryckhållfastheten.

Härdning av den förbättrade återvunna betongballasten under närvaro av CO_2 kan konsumera 30-40 g CO_2 per kg produkt (den förbättrade fina återvunna betongballasten). Detta beräknas leda till en potentiell minskning av koldioxidavtrycket i betongproduktionen med 8-10%, under förutsättningen att den naturliga sanden kan ersättas med den förbättrade fina återvunna betongballasten. Dessutom sparas andra naturresurser genom att återvunna betongballaster används.

I projektet har ett enkelt och snabbt test (4 veckor) använts för utlakning av tungmetaller ur den konstgjorda sanden. Detta inledande lakningsförsök visar på låg utlakning av metaller, men detta behöver följas upp med mer långtidstester.

Baserad på resultaten från detta projekt kan man säga att:

- Den huvudkemiska sammansättningen och innehållet av tungmetaller i bottenaska från två MSWI-anläggningar är lika, oberoende av partikelstorlekar.
- Det nuvarande askutsläppssystemet i förbränningsanläggningarna behöver vattenkylas och lagras för att sortera metaller innan bottenaska släpps ut. Den potentiellt hydrauliska kapaciteten i askan har frigjorts och hydratiseringsprodukter bildades redan i askan under lagringsperioden på grund av det fuktiga tillståndet och karboniseringsprocessen.
- Stenkulorna tillverkade av bottenaska och masugnsslagg kan förbättra bearbetbarheten/gjutbarheten hos färsk betong och motståndet hos hårdnad betong mot kloridinträngning, men med en viss minskning i tryckhållfastheten.
- Bottenaska tillsammans med masugnsslagg och alkali-aktivator kan förbättra den fina återvunna betongballasten (0-2 mm) för att göra de återvunna betongballasterna (0-4 mm) fullt applicerbar i betong (murbruk) för att ersätta den naturliga sanden utan att försämra bearbetbarheten/gjutbarheten och tryckhållfastheten.
- Både de konstgjorda stenkulorna och de förbättrade återvunna betongballasterna är lättare än de naturliga ballasterna. Detta kommer att leda till en minskning av betongvikten med cirka 12% om de naturliga ballasterna ersätts av de "gröna" ballasterna som utvecklats i detta projekt.
- Härdning under närvaro av koncentrerat CO₂ kan förbruka 30-40 g CO₂ per kg produkt (den förbättrade fina återvunna betongballasten), vilket kan leda till en potentiell minskning av koldioxidavtrycket i betongproduktionen med 8-10% om den naturliga sanden kan ersättas med de förbättrade betongballasterna, utöver de andra miljö- och ekonomiska fördelarna (besparing av naturresurser genom ersättning av återvunna betongballaster).
- Inga markant utlakade tungmetaller kan detekteras från ett enkelt lakningstest efter 4 veckor, vilket innebär ett behov av ytterligare undersökning av långtidslakningsbeteende.

Nyckelord: ballast, aska, bottenaska, slaggrus, cement, betong, avfallsförbränning, grön ballast, stenkulor.

Summary

Large volumes of bottom ash from waste incineration are generated, which are primarily used for landfill constructions. Demand for this use will decrease in the future. There is an urgent need for developing techniques that allow a safe utilization of these ashes, especially related to the goal of CO₂ neutral climate in 2045. On the other hand, concrete is by volume the most used construction material consisting of cement and aggregates, the former has a high CO₂ emission in its production whilst the latter need to consume natural resources which are becoming less and less. This project is for testing a new idea aiming to study whether bottom ashes can be used for production of aggregates with CO₂ gas as a curing and reaction medium. The project includes three tasks: 1) experimental investigation of chemical compositions and hydraulic reactivities, 2) production of green aggregates, and 3) application of the green aggregates in concrete. It was found that the contents of heavy metal elements in bottom ashes from two incineration plants are similar, independent of particle sizes. The current ash discharge system in the incineration plants needs water cooling and storage for sorting off metals before discharging bottom ashes. The potentially hydraulic capacity in the ashes has been released and hydration products were already formed in the ashes under the storage period due to the moist condition and carbonation process. A “two-step” technique has been developed to manufacture stone balls or improve the fine recycled concrete aggregate (RCA) using the ground bottom ash (GBA) together with ground granulated blast-furnace slag (GGBS) under the alkali-activation. The results show that the stone balls manufactured from the ground bottom ash and GGBS can improve the workability of fresh concrete and the resistance of hardened concrete to chloride ingress, but with a certain reduction of compressive strength. After the improvement the fine RCA became fully applicable in concrete (mortar) without impairing workability and compressive strength. Curing under a concentrated CO₂ condition may consume 30-40 g CO₂ per kg product (improved fine RCA), leading to a potential reduction of carbon footprint in concrete production by 8-10% if the natural sand can be replaced by the improved fine RCA, in addition to the other environmental and economic benefits (saving of natural resource by replacement of RCA). From this study no markedly leached heavy metals can be detected from a simple leaching test after 4 weeks, implying a need for further investigation of long-term leaching behaviour.

Keywords: Aggregate, ash, bottom ash, cement, concrete, MSWI, recycled concrete aggregate, stone balls.

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1 Background

1.1 CONCRETE

Concrete is a composite material composed of fine (0-4 mm or 0-8 mm) and coarse aggregate (4-16 mm or 8-16 mm, alternatively 8-25 mm) bonded together with a fluid paste (a mix of cement, mineral additions, and water, eventually with chemical admixtures such as superplasticizer, air entraining agent, viscosity modifier, etc.) that hardens (cures) over time. To easily cast fresh concrete mixture into the mold or framework, a good workability of fresh concrete is essential. The shape of aggregate plays an important role in workability. Spheric shape of aggregate is ideal for the best workability owing to its highest packing grade and least specific surface area. When concrete is engineered as a structural building material, due to its intrinsic weak tensile strength and cracking sensitivity, steel reinforcement is required in most cases.

Concrete production consists of a time-sensitive process in which the various ingredients of concrete are mixed to produce concrete. Depending on the final desired properties, including flowing ability as well as compressive strength of the concrete, the portions of each component as well as the mixing technique or procedure could differ. Generally, the dry ingredients are mixed initially and then the water together with preliminary quantity of chemical admixtures is added into the mix. Based on the required fresh properties of concrete mixture, the actual quantity of admixtures is often adjusted. The production process of concrete can be illustrated in Figure 1.1.



Figure 1.1. Illustration of concrete production process.

1.2 SUSTAINABILITY OF CONCRETE

Cement industry is the third largest source of anthropogenic emissions of carbon dioxide, accounting for approximately 8% of global emissions [1]. The global emissions of carbon dioxide associated with cement come from three main sources: fossil fuels, land use changes and carbonate decomposition. The largest of these is

the decomposition of carbonates [1]. It is well known that fulfillment of United Nations' Sustainable Development Goals (UN SDGs)[2] without mitigation of anthropogenic emissions of carbon dioxide is impossible (SDG 13). Although cement industry has been already active since 1999 in pursuing strategies to reduce CO₂ emissions (long before global warming became a priority), global emissions due to cement production are still increasing and the amount of cement produced in the past 65 years has increased over 30-fold [3], due to the need for our modern developed societies (SDG 11) which requires a built environment that is unimaginable without the widespread use of cement-based concrete and also no other alternative for such a huge demand! Therefore, it is a fact that our civilization has become strongly dependent on this cheap building material – concrete. Any measure which can reduce the carbon footprint in concrete production will certainly contribute to the UN SDGs.

Portland clinker substitution with supplementary cementitious materials (SCMs), has been largely introduced and practiced in many countries for the last 50 years. However, the scarcity of the most common SCMs in the near future has created new concerns. Fly ash, a waste product from coal combustion and one of the most used SCMs, will be rarely available in the future, as the coal combustion is expected to decrease due to carbon dioxide concerns. Ground granulated blast furnace slag (GGBS), another SCM, is available in low and very varying amounts, making a constant production of so called composite cements with lower CO₂ footprint [4] challenging. Therefore, seeking to find alternatives to those SCMs, several new SCMs have been introduced in the past few years, such as calcined clays [5-10], bio ashes [11-18] or steel slags [19] with high proven potentials. Nevertheless, application of alternative binders is only one of the solutions for minimizing the carbon footprint of cement production, as only a portion of the clinker can be substituted with these materials. Therefore, it is well demonstrated that total carbon neutrality can only be achieved by recapturing this “chemical” CO₂. The technologies for carbon capture and storage are being introduced in the cement and concrete industry. However, it is of great importance to seek a potential utilization for the captured CO₂ as well, and therefore, seeking techniques in which CO₂ can be consumed in favor of producing new ingredients for concrete production is of great interest.

On the other hand, natural resources for aggregates (sand and stone) become less and less available. In a long sighted view, artificial and recycled aggregate would be a solution to the shortage of natural aggregates which take up 60-70% by volume of concrete. In many countries, especially Asian, the demolished old concrete structures are often crushed to produce recycled concrete aggregate (RCA). In the past years some efforts were made in Sweden on the potential application of RCA [20]. In the literature, the RCA with size > 4 mm can be used in the new concrete production without impairing concrete quality [21]. Based on our ongoing EU project TRAC (grant No 777823, Tailor-made Recycled Aggregate Concretes), the RCA with size 2-4 mm may also be reused but it is difficult to reuse the fine part (< 2 mm) due to its high quantity of water absorption and poor particle shape, both of which impair the workability of fresh concrete. However, in the crushed concrete, the portion of this fine part can take up about 40% of the total RCA, as shown in Figure 1.2. Therefore, if we can improve the fine RCA to make it

applicable in concrete, the recycling or reuse degree of demolished concrete can significantly be increased.

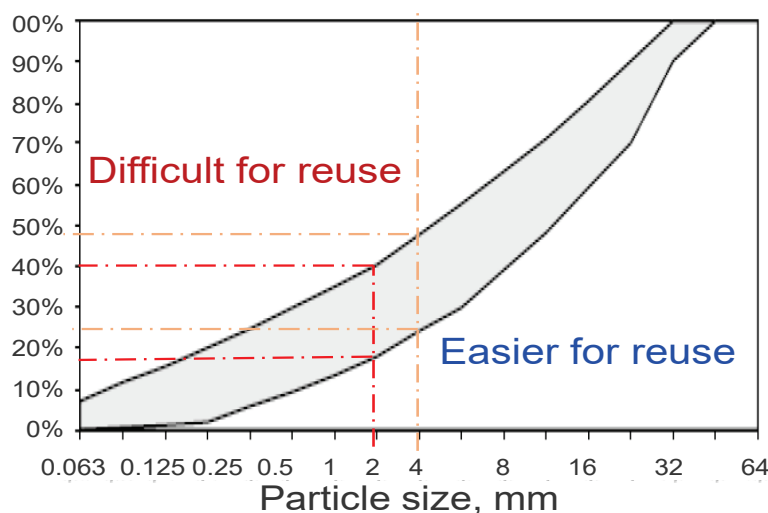


Figure 1.2 – Particle size distributions of recycled concrete aggregate (RCA). Data based on [22].

1.3 CIRCULAR ECONOMY AND UTILIZATION OF ASHES AS A BUILDING MATERIAL

With the development of sustainable societies, more and more waste-to-energy plants have risen to produce energy from municipal solid waste (MSW). Sweden is one of the pioneer countries in which MSW is incinerated to produce energy. Although the modern incineration technique can convert a major portion of MSW to energy, a significant quantity is still left in the form of bottom ash (20-25% of MSW) and fly ash (about 5% of MSW). In Sweden the quantity of MSW incineration (MSWI) ashes is about one million tons/year [23]. The major portion of the Swedish MSWI ashes is at present used for construction within landfills. With the sharpened EU regulations [24], most of the MSWI fly ashes are still classified as hazardous wastes due to their high content of heavy metals and salts, whilst the bottom ashes (about 700 000 tons/year [23]) are often classified as non-hazardous waste. The amount of MSW is increasing and the combustion of MSW for energy production will continue, whilst the number of landfills is decreasing. There is, therefore, an urgent need for developing techniques that allow a safe utilization of the MSWI ashes. As mentioned in section 1.2, any measure which can reduce the carbon footprint in concrete production will certainly contribute to the UN SDGs. If MSWI ashes could either be added to concrete as a cement replacement material or be considered as an aggregate for use in concrete, it would be better than simply be used as landfilling cover. If the process for aggregate production can be optimized with CO₂ consumption, the new manufactured aggregates would not only enhance a circular economy utilizing industrial wastes in concrete production but also benefit reduction of CO₂ as explained in the previous section. Considering the goal of CO₂ neutral climate in 2045, such a utilization can result in a large reduction of CO₂ emission, if CO₂ is utilized together with MSWI ashes.

MSWI ashes contain significant amounts of chemically reactive and potentially hydraulic composites consisting of oxides, i.e. SiO_2 , CaO and Al_2O_3 , which can be used as cementitious materials if properly activated under suitable activation conditions. On the other hand, these reactive composites can, if not properly hydrated, induce cracks due to later expansive reactions in the hardened concrete. Owing to the demand for sustainable waste management, the research interest on the use of MSWI ashes in concrete is globally high, especially in the countries where the space for landfilling is limited. Earlier research efforts in this area were focused on the use of MSWI ashes for partial replacement of binder and aggregate [25-28]. Pera et al. [26] pointed in their study out that, when directly introduced into concrete, MSWI bottom ash led to swelling and cracking in concrete due to the metallic aluminium content in the ash. The aluminium metal reduces the water and forms hydrogen gas in the alkaline pore solution in the concrete. They suggested that a pre-treatment was needed before the ash could be used in concrete. In Germany, Müller and Rübner [27] investigated the concrete aggregated with MSWI bottom ash and found the cracking and spalling problems in concrete due to the delayed aluminium reaction. In China, Zhang and Zhao [25] evaluated the mechanical properties of concrete mixtures, in which the coarse aggregate was partially replaced with pre-washed MSWI bottom ash. Their results show that bottom ash reduced the compressive strength and elastic modulus when used as a replacement for coarse aggregate. Recently, a pilot scale project was initiated at RISE CBI for utilization of pulp mill wastes in cement-based materials as a case study in cooperation with Södra (financed by Energimyndigheten). In this project, up to 50 different biomass ash samples including both bottom and fly ashes from three different incineration plants were collected and analyzed [29]. The results show that the biomass ashes varied within a reasonable range of chemical composition with respect to both time and location, and the pozzolanic activity as well as activity index of the bio-fly ashes is close to the border of acceptance according to SS-EN 196-5 and ASTM C311 standards, indicating good potentials for further investigations. In U.K., due to the need for new sources of SCMs, Lynn et al. [30,31] studied MSWI bottom ash for use as a cement component in concrete. Through their critical assessment of the characteristics of MSWI bottom ash they concluded that MSWI bottom ash can be incorporated at minor contents as raw feed in cement clinker production. In Netherlands, Tang [32] studied the MSWI bottom ashes after thermal and milling treatments and found that the thermal treatment combined with slow milling can reduce the negative influence of bottom ash on cement hydration and remove the metallic aluminium.

It can be seen from the above referenced papers and reports that the usability of MSWI ashes in concrete is still limited to a small amount of replacement for Portland cement as SCM, aggregate or filler based on some trial and error approaches. One of the reasons for low scale utilization of MSWI ashes as building materials is the fact that the ashes often contain a certain amount of metallic aluminium, which is detrimental if directly used in concrete as an important and durable construction material.

Different from the previous researches by means of simple addition of ashes in concrete, our new idea is to identify chemical compositions including contents of harmful substances and pozzolanic reactivities of bottom ashes with various

particle sizes, and utilize the less harmful portions of bottom ashes, the portion with pozzolanic reactivities as cementitious materials and the relative inert portion as “seeds” for production of stone-like balls, which are cured by CO₂ gas from e.g. cement production. During the curing, CO₂ will react with calcium to form calcium carbonate. In this way, the metallic aluminium will react with alkali solution and simply introduce air pores in the balls, whilst the carbonation will only reduce the alkalinity of the balls. When these balls are used in concrete as aggregates, the defects inside the balls will not affect the properties of new cementitious matrix in concrete with respect to the transport and steel protection properties. Therefore, this new idea should lead to a promising solution to both recycling industry (value-added use of bottom ashes) and construction (including cement) industry (value-added use of emitted CO₂).

To test the above new idea, Energiforsk supported this pilot project aiming to study whether bottom ashes can be used for production of aggregate balls, where CO₂ gas is used as a curing and reaction medium.

The objectives of the project through the experimental investigations, are:

- to identify the contents of harmful substances and pozzolanic reactivities of bottom ashes with various particle sizes under different alkaline environments;
- to demonstrate the feasibility of utilizing less harmful portions of bottom ashes for production of cementitious balls with carbon dioxide gas as curing/reacting media; and
- to demonstrate the feasibility of applying the produced cementitious balls as aggregate in concrete production.

The project was led by Chalmers University of Technology, in the close cooperation with industrial partners including Stena Recycling International AB (Stena), Renova AB (Renova), Cementa AB and the C-lab at Thomas Concrete Group AB (TCG).

This report presents the findings from the experimental investigations.

2 Bottom ashes and treatment methods

2.1 BOTTOM ASHES

The bottom ashes used in this study were delivered by two incineration plants, R and S. The ashes are noted as follows:

- R0-10: Slaggrus fint 0-10 mm from R, and
- S0-10: Slaggrus fint 0-10 mm from S.

According to the information supplied by the ash producers, the bottom ashes were from incinerators with a mix of household and industrial wastes. The ashes were stored in the ash accumulators for several months before separation/sorting off metals. Afterwards the separated/sorted ashes were stored for about half a year before delivery to Chalmers for use in the project.

2.2 CHARACTERIZATION OF ASHES

2.2.1 Physical properties

The moisture content in each ash (measured by the weight loss between the as-received condition and after dried at 105 °C) was 15.3% and 14.4% for R0-10 and S0-10, respectively. The particle size distributions (PSD) of ashes (measured according to EN 933-1) are shown in Figure 2.1.

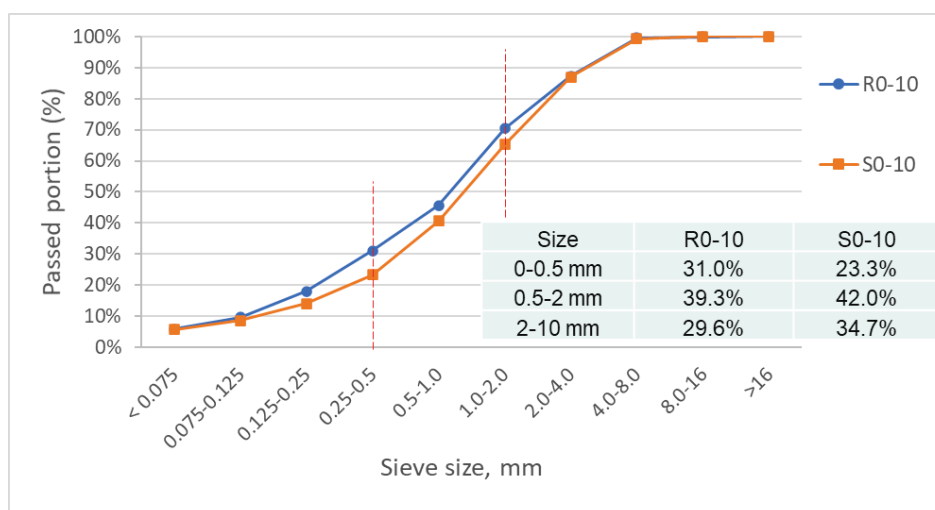


Figure 2.1 – Particle size distributions of bottom ashes.

Based on the PSD, each ash was divided into three portions with the particle sizes 0-0.5 mm (noted as 005), 0.5-2 mm (noted as 052) and 2-10 mm (noted as 210). Hereafter the symbols R005, S005, etc., will represent the ash with size 0-0.5 mm from R and S, respectively.

2.2.2 Chemical composition

From the above portions a small quantity of ash (about 50 grams) was ground in a pulverizer of ring-puck type to the particle size <0.25 mm. About 10 grams of each pulverized portion was sent to ALS Scandinavia AB for analysis of chemical composition. The rest of the pulverized samples were kept in the sealed test tubes for testing hydraulic properties as will be described later in section 2.3.

According to the methods description supplied by ALS, the samples were analysed using ICP-SFMS for determination of chemical elements according to SS EN ISO 17294-2: 2016 and EPA-method 200.8: 2014. The results reported by ALS were, however, in terms of oxides for the major elements, which should be estimated from the elements determined by ICP. Because we do not know if these major elements existed in the ashes were in the form of oxides, hydroxides or carbonates, these oxide contents were calculated back to the element contents. The results from the chemical analysis are shown in Figures 2.2 and 2.3, whilst the data reported by ALS are listed in Appendix 1.

From Figures 2.2 and 2.3 we can see that both bottom ashes have similar chemical composition, that is, the ashes contain 13-20% silicon, about 12-17% calcium, 5.5-6.5% aluminium and 4.4-5.9% iron. No significant difference appears in the three ranges of particle sizes, except for the mercury contents, which is higher as particle size is smaller.



Figure 2.2 – Major element contents in bottom ash R and S.

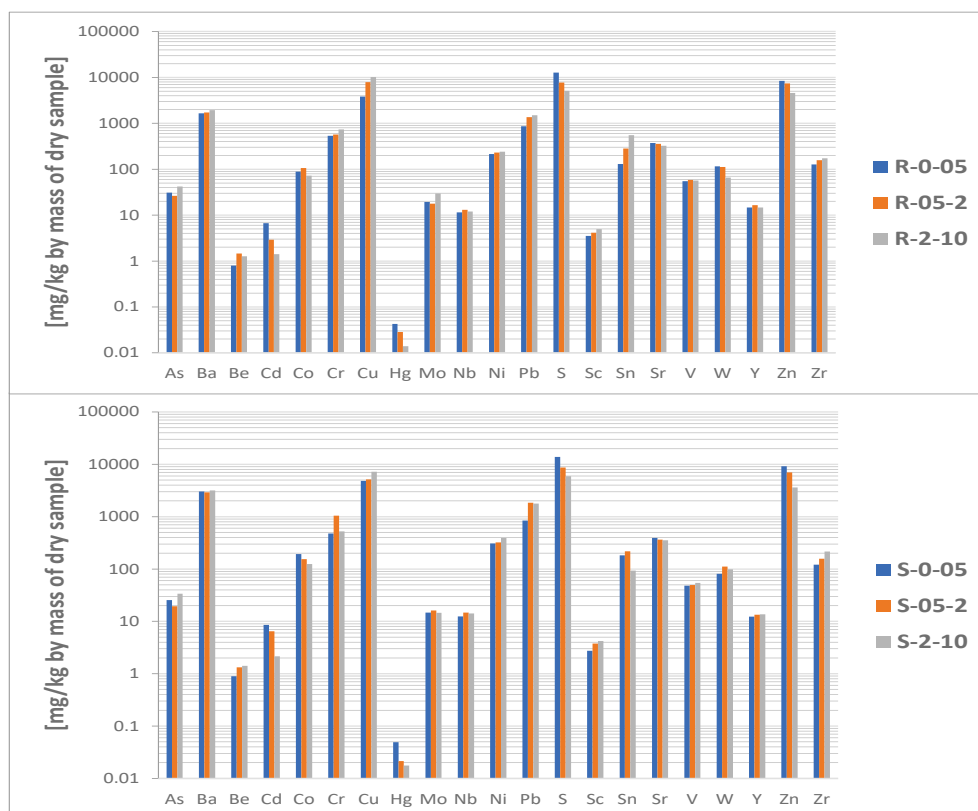


Figure 2.3 – Minor and trace element contents in bottom ashes R and S.

2.3 HYDRAULIC PROPERTIES OF BOTTOM ASHES

To form a strong solid the ashes should have certain hydraulic properties to bind different particles together. Therefore, it is important to evaluate their hydraulic properties. In this project the bottom ashes were tested based on a method reported by Glikson and Menéndez [33] with certain modifications to suit the ashes in this project. The method includes the following procedures:

1. Blend about 2 g powder sample in a 50 ml centrifugation tube with 40 g NaOH (1 M);
Assemble the tightly sealed tubes on a rotator and keep them rotating at 12 rpm at 40 °C for 7 days;
3. Centrifugate the test tubes in a spinner at 4000 rpm for 5 min to separate the exceed liquid from the sample;
4. Replace the exceed liquid with isopropanol and stir the mix firstly by suitable tool (e.g. a spatula) and shaking and then rotating on the rotator at 12 rpm for about 1 hour to stop the hydration process;
5. Vacuum filtrate the sample using a Büchner funnel with filter paper and rinse the residue using approximately 20 ml of isopropanol followed with approximately 20 ml of diethyl ether;
6. Transfer the residue into a crucible (pre-weighed and noted as m_{crucible}) using a spoon and dry it in a vacuum oven at 40 °C for about 10 minutes;
7. Weigh the sample (noted as $m_{40^\circ\text{C}}$) and dry it at 105 °C overnight;

8. Weigh the sample (noted as $m_{105^{\circ}\text{C}}$) after transferring the sample to a desiccator for cooling down to the room temperature;
9. Heat the sample in a high temperature oven at a rate of 80 °C/h to 350 °C, keep it at 350 °C for 2 hours and decrease the temperature at a rate of 80 °C/h to 105 °C; and
10. Weigh the sample (noted as $m_{350^{\circ}\text{C}}$) after transferring the sample to a desiccator for cooling down to the room temperature.

The relative quantity of chemically bound water by the hydration products can then be estimated by the following equation:

$$W_h = \frac{m_{105^{\circ}\text{C}} - m_{350^{\circ}\text{C}}}{m_{105^{\circ}\text{C}} - m_{\text{crusible}}} \times 100 \quad \% \quad (1)$$

To check the initial hydration products in the ashes, the chemically untreated raw samples were also subjected to procedures 7) to 10).

The results are shown in Figure 2.4. It seems that the chemical treatment with the 1 M NaOH solution did not produce more chemically bound water in each sample. After consultation with the ash suppliers it was realized that under the current ash discharge system in the incineration plants the bottom ashes have to be water-cooled and stored in the ash accumulator for a certain time before sorting off metals and then stored in a relatively moist condition for months before being transported to the landfilling field as covering materials. During these two storages the potentially hydraulic capacity in the ashes has been released and hydration products were already formed in the ashes.

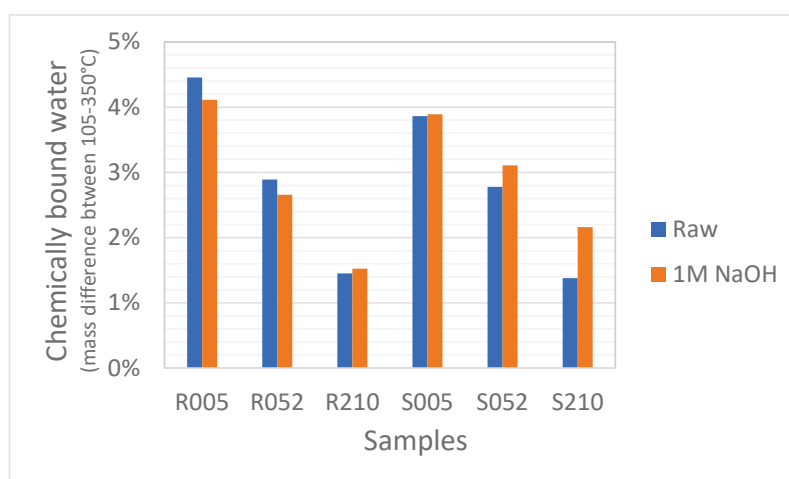


Figure 2.4 – Chemically bound water content in the bottom ashes.

2.4 GROUND BOTTOM ASHES (GBA)

To examine the potential application of these already hydrated ashes as green aggregates, 0-10 mm fraction of the bottom ashes were firstly dried at 105 °C to a constant mass (for about 2-3 days) and then ground using a steel ball miller at the

C-lab of Thomas Concrete Group AB for about 24 hours to pass the sieve of size 0.25 mm. This grinding process is necessary because the large particles may still contain some latent hydration properties which react slowly in the hardened concrete and create harmful cracks at the later age.

The ground bottom ashes (GBA) are noted as R025 and S025, Figure 2.5 shows their particle size distributions determined using a soil PSD analyser PARIO with the dispersant (33 g sodium hexametaphosphate and 7 g sodium carbonate according to SS-ISO 11277:2020). This method is based Stock's law to determine the weight of the dropped particles whose dropping velocity are dependent on their size. The larger the particle size is, the quicker the particles will drop down to the scale. In Figure 2.5, the large portion of superfine particles (about 30% $<2.5 \mu\text{m}$, which is finer than silica fume!) seems not true, possibly due to a strong suspension of ash particles in the solution which did not follow Stock's law as the method is based on. As shown in Figure 2.4, the ashes contain a certain amount of hydration products, which are strongly hydrophilic and can attract water molecules around each particle to form gels, which suspend in the solution due to a reduced density by the water molecules and thus dropped down very slowly. Therefore, the soil PSD analyser PARIO may not be suitable for measurement of bottom ashes.

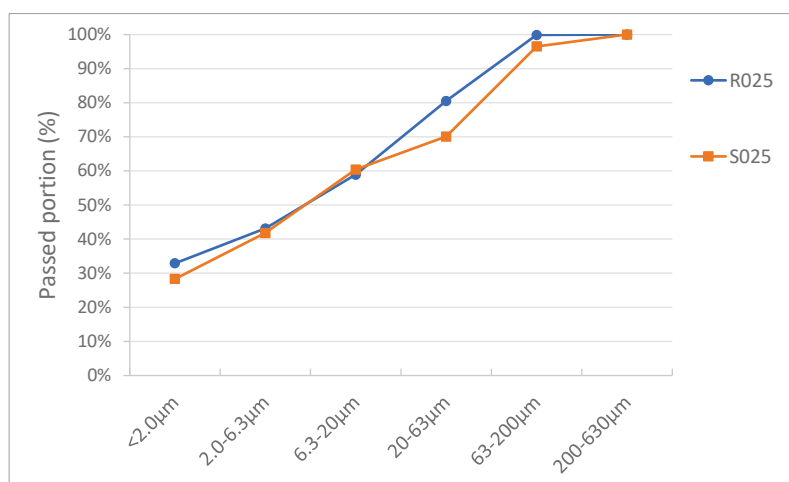


Figure 2.5 – Particle size distribution of the ground bottom ashes.

2.5 OTHER MATERIALS

In this project the following materials were used in the treatment of bottom ashes:

Ground granulated blast furnace slag (GGBS), supplied by Thomas Concrete Group AB (TCG), for improving the hydraulic property of bottom ashes. Detailed information about physical properties and chemical compositions of the GGBS can be found in [34].

- Alkali-activator, for activating the hydration of bottom ashes and GGBS. It was a sodium silicate solution with the molar ratio of $\text{SiO}_2:\text{Na}_2\text{O} = 1$ and the solid content of 30% by mass, prepared by ourself in the laboratory, using the

commercial waterglass N2 ($\text{SiO}_2:\text{Na}_2\text{O} = 3.35$ and solid content = 36.1%) supplied by SIBELCO Nordic AB and the sodium hydroxide pellet (98%, Fisher Scientific Gtf AB), together with demineralized water.

- Natural sand, type “Fogsand”, produced by St. Eriks AB, as nucleator of manufactured aggregate using bottom ashes. The sand was dried in the laboratory room for more than one month before use.
- The fine recycled concrete aggregate (RCA), as an example of poor shaped fine aggregates to be refined by the mixture of bottom ashes and GGBS. The RCA was obtained from a demolished Swedish road bridge (Gullspång bridge built in 1935), through a Swedish research project “Recycled concrete aggregates in climate-neutral structural applications” under the program “InfraSweden 2030”. Owing to its high moisture content (9.3% by mass), the RCA was dried at 105 °C to a constant mass (for about 2-3 days) before use. The dry particle density of RCA is 2100 kg/m³.

3 Manufacturing green aggregate

3.1 STONE BALLS

3.1.1 Manufacturing stone balls

As mentioned in section 1.1, spheric shape of aggregate will be the best one for the workability of fresh concrete. It would be a good idea if the bottom ashes can be used for manufacturing the stone-like balls which can be used in concrete as coarse aggregate. This manufacturing process is an innovative technique to be developed in this project. Therefore, it is difficult to compare this new process with previous works in terms of details of manufacturing technique. The idea is to manufacture stone balls which can be added to the concrete as aggregate in which both utilization of the ashes as well as consumption of CO₂ is considered. There are very limited published papers dealing with the manufacture of artificial stone balls using cementitious materials [35,36], although industrial machines are available for pellets or balls. Owing to the financial limitation, we were forced to try ourselves to find suitable machines for manufacturing stone balls in the laboratory.

Two types of rotation machine were tried for manufacturing stone balls:

- a small concrete mixer (30 litres) as shown in Figure 3.1a; and
- a self-made mixer based on a plastic barrel installed with five triangle wooden strips as shown in Figure 3.1b.

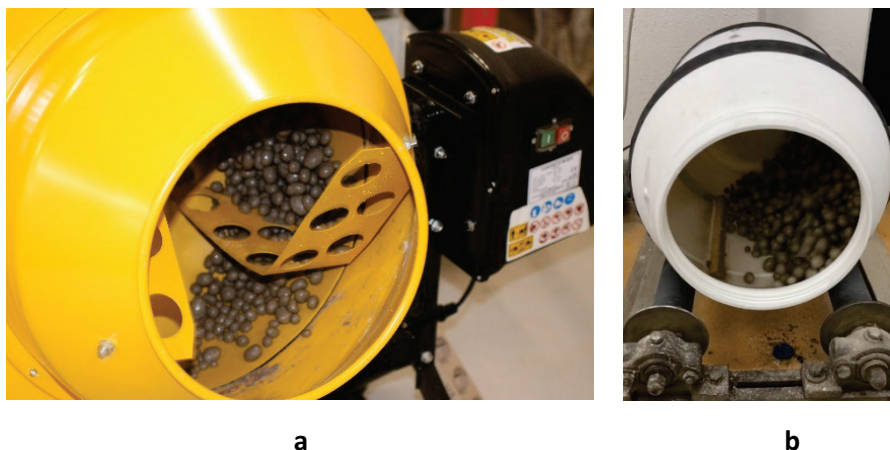


Figure 3.1 – Rotation machines for ball manufacturing.

After several trials it has been realized that a successful formation of balls is dependent on a number of factors, including powder and liquid content in the mixture, rotation rate, addition of the dry mixture, etc. From the preliminary results it was found that the balls were broken after hardening, as shown in Figure 3.2, to a great extent due to the metallic aluminium in the ashes, which releases hydrogen gas under the alkaline condition. This means that a pre-treatment has

been added to get rid of this gas before the formation of balls. On the other hand, the extensive evaporation of moisture in the mixture should be avoided under the gas release period. Therefore, the mixer must be sealed under the gas release period. The concrete mixer cannot be sealed for this purpose. Therefore, the self-made mixer was finally chosen for manufacturing stone balls. Figure 3.3 shows the self-made mixer with a lock at the centre of which a stopcock is mounted for release of gas.



Figure 3.2 – Cracking probably due to the metallic aluminium (release H_2 gas under the alkaline environment).

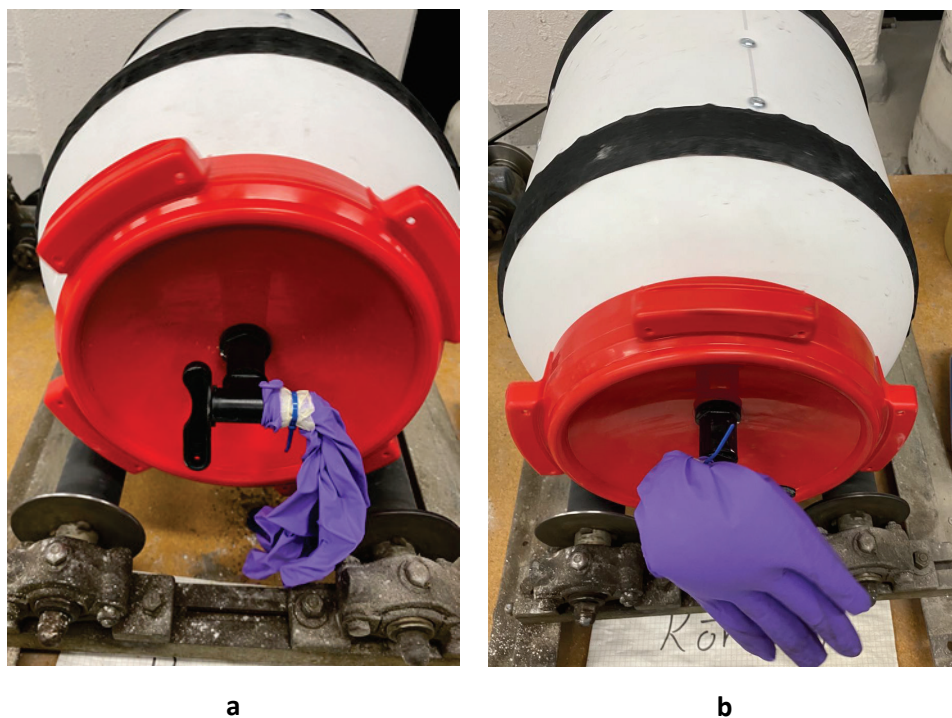


Figure 3.3 – Self-made mixer with lock at the centre of which a stopcock is mounted for release of gas. a: before gas release; and b: after gas release.

The typical proportions of materials for manufacturing stone balls, as concluded in this study after several trials, are listed in Table 3.1 and the “two-step” manufacturing procedures are summarized as follows:

1. Weigh the materials according to Table 3.1;
2. Pre-mix the dry materials of M1 in the standard cement mortar mixer at the low rotation rate for 60 sec;
3. Add the alkali-activator of M1 to the mixture and mix it at the low rotation rate for 60 sec;
4. Fill the mixture to the self-made mixer through a sieve of 4 mm and break those parts large than 4 mm by suitable tool to let them pass the sieve into the mixer;
Seal the mixer with the lock on which there is a stopcock for gas release (Figure 3.3);
6. Rotate the mixture at about 20 rpm for 2 hours for thorough gas release;
Remove the lock and add the dry materials of M2 to the mixture;
8. Rotate the mixture at about 25 rpm for 1-2 min and add the alkali-activator of M2 to the mixture under the rotation condition;
9. If it appears too large lumps or balls, stop the rotation and break down the large lumps or balls by suitable tools;
10. Continue rotation and, when the balls become reasonably shaped, spread the dry materials of M3 with a small portion to the balls to protect the balls from further aggregation and at the same time to absorb the exceed moisture on the surfaces of balls; and

11. After all the materials of M3 were added, stop rotation and transfer the balls into a plastic bag for curing.

The above procedures 1 to 6 are designed for releasing the gas from the ash as Step 1 and the rest procedures (7 to 11) are for ball formation as Step 2.

Table 3.1 – Proportions of materials (in grams) for manufacturing stone balls.

	M1	M2	M3	Note
GBA	300			
GGBS	300	300	250	
Fogsand	1200	600	500	
Alkali-activator	200/225	250/265	-/-	For R025/S025, respectively

It can be seen from Table 3.1 that about 10% more liquid, i.e. alkali-activator, was needed for S025 to reach a workability similar as R025 for manufacturing stone balls. As shown in Figure 2.5, there is no markedly difference in PSD between two ashes. From Figure 2.4 we can see that the R ash revealed a little more hydration products which needs less water for lubrication. This could be the reason why S025 ash needs more liquid in the mixture

3.1.2 Curing stone balls

After the balls have been transferred into the plastic bag, the bag was filled with CO₂ and sealed with its zip, as shown in Figure 3.4. The sealed bag was placed in an oven for curing at 50 °C for 48 hours, and then stored in the laboratory room at 20-22 °C for further curing (1-4 weeks due to different batches of manufacturing) until transported to TCG for concrete casting. Under the room curing period the bags were re-filled with CO₂ time to time.

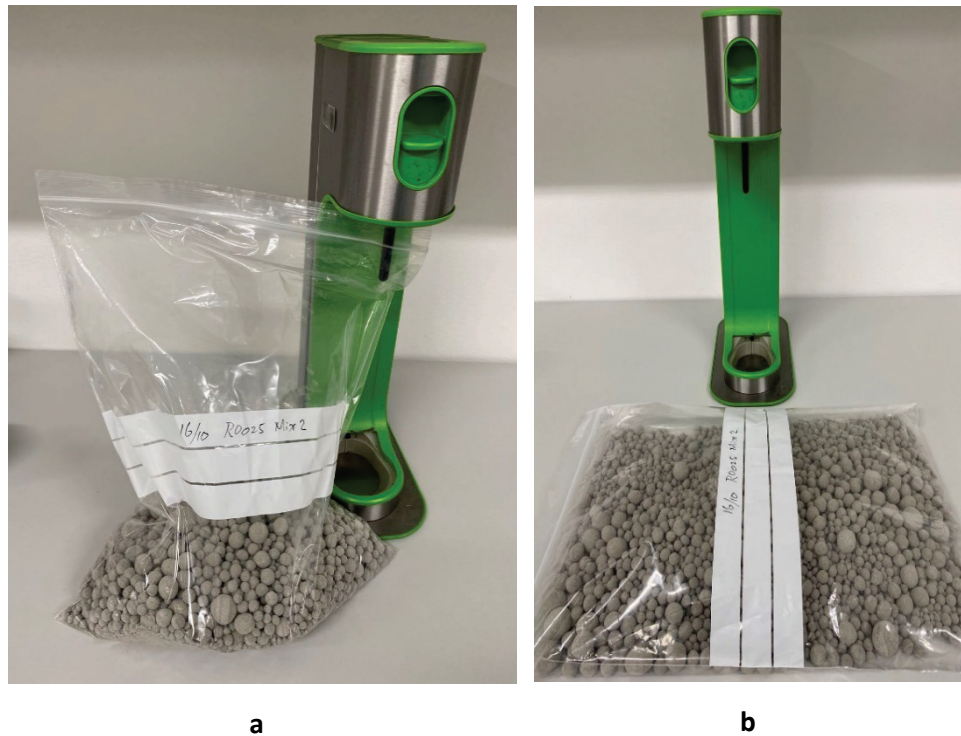


Figure 3.4 – CO₂ filling (a) and filled (b).

3.1.3 Particle size and density of stone balls

The particle sizes of stone balls varied batch to batch, strongly dependent on the procedures 9) and 10) described in 3.1.1, which to a great extent involved operator's visual judgement and handwork for breaking down the large lumps or balls. Therefore, no individual measurement of particle size distribution was carried out. Because the fine aggregate (sand) in Sweden is often 0-8 mm, for the purpose of use as coarse aggregate (size >8 mm) in concrete, the balls were separated by a sieve of 8 mm. The most portion of the balls over the sieve is in the range of 8-16 mm, with a small portion of 16-25 mm.

A small portion of stone balls with sizes 10-12 mm was used for determination of particle density based on the mass of balls under the natural condition after curing in the plastic bag, that is, without external drying. The mass of stone balls was measured in the air (noted as m_{air}) and in the water (noted as m_{water}), respectively. The particle density is calculated by Equation (2).

$$\rho_{\text{ball}} = \frac{m_{\text{air}}}{m_{\text{air}} - m_{\text{water}}} \cdot \rho_{\text{water}} \quad (2)$$

where ρ represents the density.

The measured values are (2170 ± 141) kg/m³ for the balls made from R025 and (2260 ± 298) kg/m³ for the balls made from S025, both of which are lighter than the natural aggregate (2650-2700 kg/m³), implying less mass quantity to be used in concrete to reach the same volume.

3.1.4 Compressive strength of stone balls

The compressive strength of stone balls (sizes 8-16 mm) was estimated based on the principle of the California Bearing Ratio Test [37], that is, a single ball is subjected to a compression force until broken and the compressive strength is calculated by the following equation.

$$f_c = \frac{2.8F}{\pi d} \quad (3)$$

where f_c is the compressive strength (MPa), F is the failure force (N), and d is the diameter of the ball (mm).

In this project a manually operative compression machine was used for testing the failure force of the stone ball, as shown in Figure 3.5.

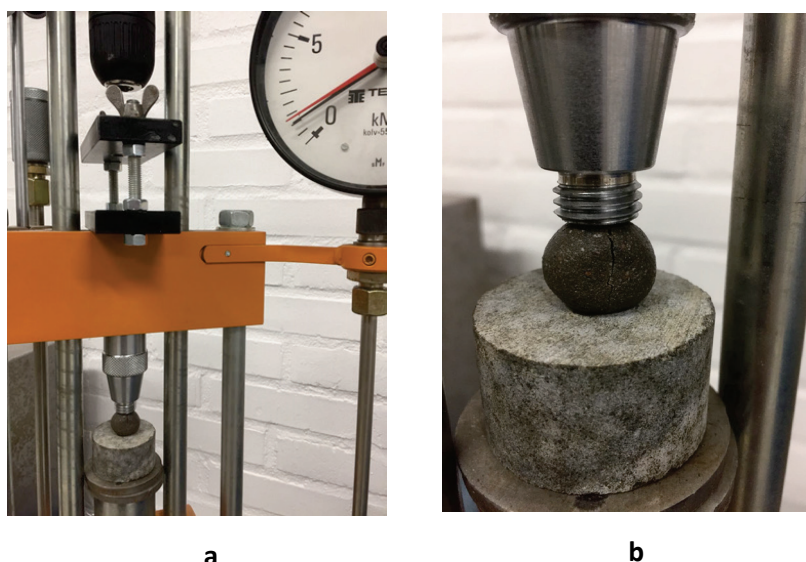


Figure 3.5 – Testing for compressive strength of stone balls. a: Overview of the test arrangement; and b: close view of the broken ball.

The test results are summarized in Table 3.2, where GGBS represents the stone balls manufactured by GGBS only, that is, the amount of GBA in Table 3.1 was replaced by GGBS and the amount of alkali-activator was the same as for R025.

Table 3.2 – Measured compressive strength of stone balls in MPa.

	Mean	Std. dev.	Test number
GGBS	8.89	1.81	8
R025	5.64	1.42	19
S025	6.42	1.51	12
C10G20CH3*	2.26	≈0.5	6
C20G20CH3*	2.98	≈0.15	6

* Data from [36], where C, G, CH denote cement, GGBS and $\text{Ca}(\text{OH})_2$, and the numbers denote percentage of the respective material in their mixes.

It can be seen from Table 3.2 that the compressive strength of R025 is lower than that of S025, probably due to the higher liquid (more alkali-activator) content in S025, as listed in Table 3.1. The strength of both R025 and S025 is lower than that of GGBS, due to the lower hydraulic capacity of the bottom ashes. However, the values in Table 3.2 are markedly higher than those reported by Jiang et al. [36]. Therefore, the balls we produced should have reasonably good quality compared with the ones in the literature.

3.2 IMPROVEMENT OF THE FINE RCA

As mentioned in section 1.2, if the fine particles from the crushed concrete can be utilized the recycling or reuse degree of demolished concrete can significantly be increased. Therefore, we tried to use GBA to improve the fine RCA.

3.2.1 Improving process

The manufacturing procedures for improving the fine RCA are similar as procedures 1) to 6) in manufacturing stone balls (see 3.1.1), but the mix proportions are as listed in Table 3.3, where GRCA in the last column denotes the mix of GGBS and fine RCA.

Table 3.3 – Proportions of materials (in grams) for improving the fine RCA.

	R025RCA	S025RCA	GRCA
GBA	300	300	0
GGBS	300	300	400
Fine RCA	1200	1200	1200
Alkali-activator	240	260	245

3.2.2 Curing conditions

The curing conditions were similar as described in 3.1.2, that is, under CO₂ and at the elevated temperature (50 °C) for about 48 hours and then in the laboratory room within the sealed plastic bag filled with CO₂ until been used for casting specimens.

3.2.3 Particle size distributions and particle density of the improved RCA

The particle size distributions of the improved RCA were measured by the sieve method after cured at the elevated temperature and cooled down to the room temperature. The results are shown in Figure 3.6, where “Funk & Dinger” indicates an ideal grading curve based on the model proposed by Funk and Dinger [38], that is,

$$PD = \frac{D^q - D_{\min}^q}{D_{\max}^q - D_{\min}^q} \quad (4)$$

with $D_{\max} = 4$ mm, $D_{\min} = 0.125$ mm and the exponent $q = 0.3$.

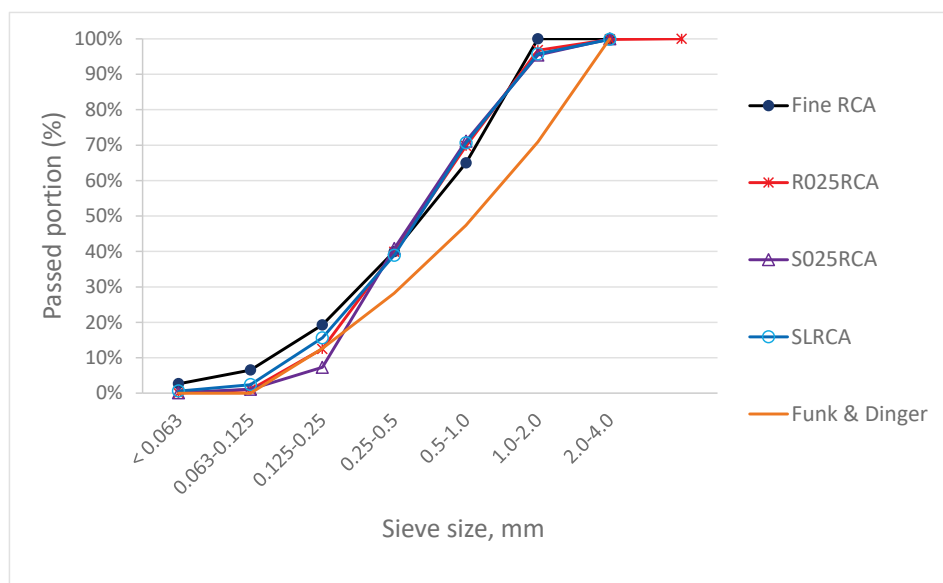


Figure 3.6 – Particle size distributions of the improved RCA.

It can be seen from the figure that, after the improvement the fine particles (< 0.5 mm) became less whilst the large particles (> 0.5 mm) became more.

Owing to the limitation of equipment, only the particles > 1 mm were used for measurement of the particle density in the same way as described in 3.1.3, that is, under the natural conditions without drying. The results are listed in Table 3.4. Compared with the natural sand (density 2650 kg/m³), all these improved RCAs are about 12% lighter, implying less weight when producing the same volume of concrete.

Table 3.4 – Particle density of the improved RCA (size 1-4 mm).

Sample	R025RCA	S025RCA	GRCA
Density, kg/m ³	2310	2270	2330

4 Applications of green aggregate

4.1 CONCRETE WITH STONE BALLS

4.1.1 Concrete specimens

The stone balls of sizes 8-25 mm manufactured at Chalmers laboratory were transferred to the C-lab at TCG where they were used as coarse aggregate in concrete mixes with the strength class C35/45 (compressive strength at 28 days ³ 35 MPa for cylindrical specimens or ³ 45 MPa for cubic specimens). The goal for the workability of fresh concrete was set at 230 mm (slump value), by adjusting the dosage of superplasticizer (BASF Glenium 51/18). The mix proportions of concrete are shown in Table 4.1, where it can be seen that the mixes with stone balls need less amount of superplasticizer to reach the similar workability.

Based on the quantity of the stone balls (around 10 kg per type of GBA), about 14 litres of concrete were mixed and 8 cylindrical specimens of size $\varnothing 100 \times 200$ mm cast. The specimens were demoulded after cured for 24 hrs under the covered condition and then cured in the water until testing for compressive strength (28 and 56 days) in accordance with EN 12390-3 and chloride migration coefficient (56 days) by the RCM test in accordance with NT BUILD 492 or prEN 12390-18.

Table 4.1 – Mix proportions of concrete

Materials	Ref	R025	S025
Byggcement (CEM II/A-LL, 42.5 R), kg/m ³	335	335	335
Limestone filler (Limus 40), kg/m ³	50	50	50
Natural sand (0-4 mm, Eurosand), kg/m ³	713.7	714.8	714.9
Crushed sand (0-6 mm, Vikan), kg/m ³	286.7	287.2	287.2
Crushed stone (8-16, Vikan), kg/m ³	815	-	-
Stone balls from R025 (8-25), kg/m ³	-	665	-
Stone balls from S025 (8-25), kg/m ³	-	-	665
Water, kg/m ³	184.3	184.3	184.3
Water-binder ratio	0.55	0.55	0.55
Superplasticizer (Glenium 51/18), % by mass of cement	1.0	0.65	0.64

4.1.2 Test results

The test results are shown in Figures 4.1 to 4.3. It can be summarized that the concrete cast with stone balls containing ash as coarse aggregate revealed a lower compressive strength, with a lower density but also a lower chloride migration coefficient.

The lower density is surely attributed to the lower particle density of the stone balls (about 2200 kg/m³) compared with the density of crushed stone (about 2700 kg/m³), due to the air bubbles exist in the man-made stone balls, as shown in Figure 4.4. These air bubbles lead to a low particle strength as listed in Table 3.2, which may lead to a lower strength of concrete. In this case the stone particles

should become broken under the compression. The observation after the compression test (Figure 4.5) show, however, that the most stone balls are kept unbroken and the failures occurred at the interfaces between the stone balls and the mortar matrix.

Normally the chloride migration coefficient should increase as the strength decreases. The results in Figure 4.3 show an opposite tendency, that is, the chloride migration coefficient of concrete with the man-made stone balls is lower than the reference concrete. Figure 4.6 shows the chloride penetration fronts in Ref- and R025-concrete (S025-concrete has the same penetration front as R025-concrete) after the migration test. It seems that the stone balls blocked chloride penetration, probably due to the fact that alkali-activated GGBS has stronger chloride binding, which has a braking effect on chloride transport. From Figure 4.6b no weak interface (e.g. crack) can be seen between the balls and the matrix. The lower strength of the concrete with the stone balls is probably due to the lower elastic modulus of the stone balls compared with the natural aggregate.

Based on the results we can conclude that the stone balls containing ash as coarse aggregate can improve the workability of fresh concrete thanks to their spheric shape and the resistance of hardened concrete to chloride ingress thanks to their higher chloride binding capacity. Therefore, they should be applicable in concrete for optimization of mix proportioning by considering workability, strength and durability.

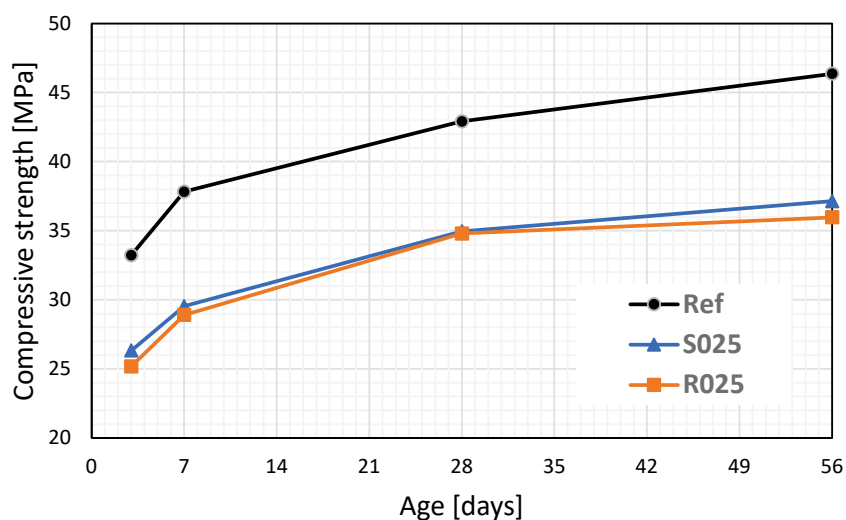


Figure 4.1 – Compressive strengths of concrete specimens.

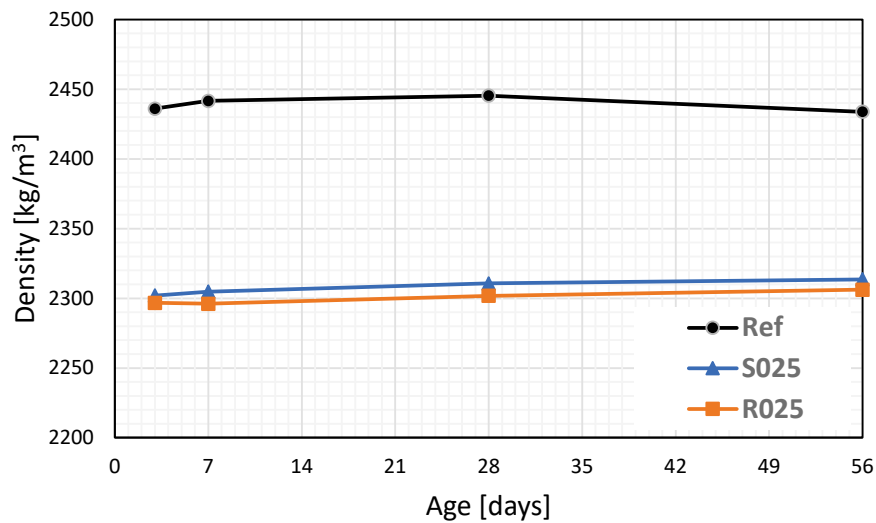


Figure 4.2 – Density of concrete specimens.

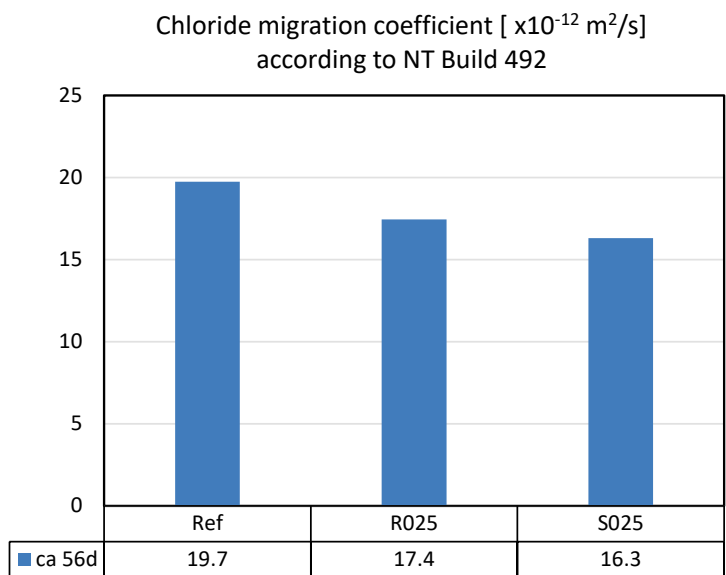


Figure 4.3 – Chloride migration coefficient of concrete specimens.



Figure 4.4 – Air bubbles inside the stone balls made from R025 GBA.



Figure 4.5 – Cross-sections of concrete after compression test.



Figure 4.6 – Chloride penetration fronts in concrete after migration test.

4.2 MORTAR WITH RCA

4.2.1 Mortar specimens

Owing the limited quantity of the improved RCA, standard mortar specimens with size 160×40×40 mm were cast for evaluating the effect of the improved RCA on the strength development. In the proportioning, the portions between aggregates with different sizes were selected in such a manner that the PSD is close to grading curve “Funk & Dinger” as shown in Figure 3.6. Because there already exists certain amount of water in the improved RCA (about 8% by mass when dried at 80 °C, and about 6% when dried at 60 °C), the mixing water was reduced to reach similar workability for casting. The final mix proportions are listed in Table 4.2.

Table 4.2 – Mix proportions of mortar in grams

Materials	Ref	S025RCA1	S025RCA2	R025RCA1	R025RCA2	GRCA
Byggcement (CEM II/A-LL, 42.5 R)	450	450	450	450	450	450
Natural sand (0-4 mm)	1350					
RCA (2-4 mm)		365	365	365	365	365

Materials	Ref	S025RCA1	S025RCA2	R025RCA1	R025RCA2	GRCA
Improved RCA with S025	-	850	850	-	-	-
Improved RCA with R025	-	-	-	850	850	
Improved RCA with GGBS	-	-	-			850
Water	225	195.3	208	208	216.5	220
Considered water content in the improved RCA, mass%	-	3.5%	2%	2%	1%	0.59%

The specimens were demoulded after cured for 24 hrs under the covered condition and then cured in the water until testing for flexural and compressive strength (at the age of 2, 7 and 28 days, respectively) in accordance with EN 196-1, but with a small number of specimens (one for flexural strength and two for compressive strength) due to the limited quantity of the improved RCA.

4.2.2 Test results

The results from the mortar tests are shown in Figures 4.7 to 4.9, where the horizontal lines indicate the reference values. The flexural strength of the mortars with RCA is in general lower than that of the reference mortar with natural sand, whilst the compressive strength of the mortars with RCA is close to that of the reference mortar. The mortar with RCA is generally lighter than the reference mortar (by about 150 kg/m³), mainly owing to the lower particle density of RCA (about 2300 kg/m³) compared with the density of natural sand (2650 kg/m³). Although the weight reduction of mortar is only about 6.5%, the total weight reduction may reach about 12% if the artificial stone balls containing ash as coarse aggregate in concrete, as shown in Figure 4.2, where it also appears a weight reduction by about 150 kg/m³ thanks to the use of stone balls. This reduced weight can certainly contribute to the reduction of carbon footprint in concrete production through the reduced materials and transportation costs.

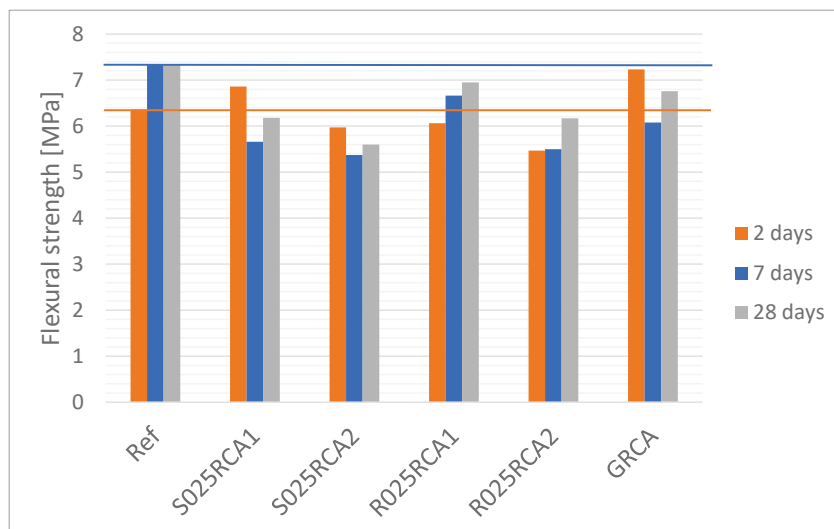


Figure 4.7 – Flexural strength of mortar.

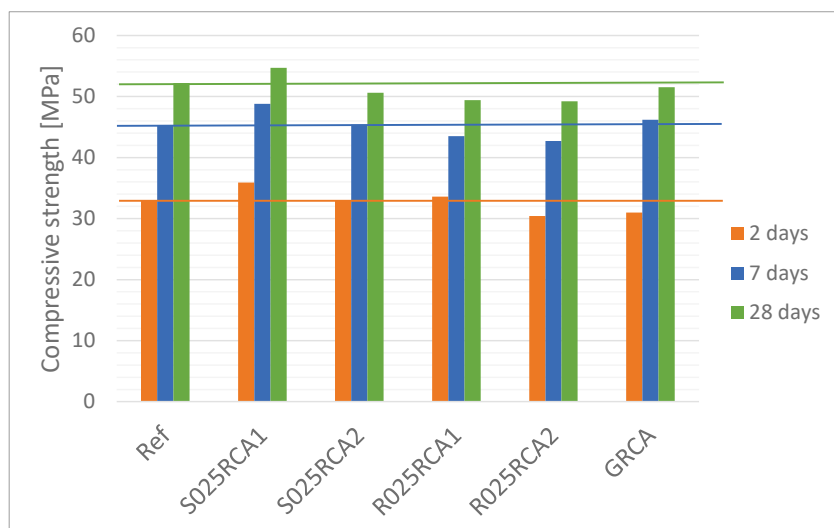


Figure 4.8 – Compressive strength of mortar.

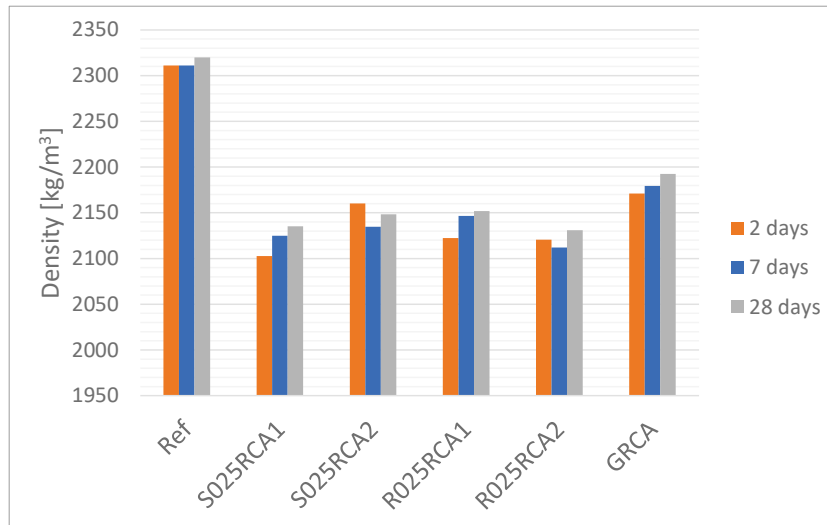


Figure 4.9 – Density of mortar.

4.3 CONSUMPTION OF CARBON DIOXIDE IN CURING

Because the water glass (sodium silicate) was used for alkali-activation, the carbonation products may contain both calcium and sodium carbonates. The conventional method based on thermogravimetry in this case is not applicable. Therefore, an acidification method was adopted for measuring the gas release. The experimental setup is illustrated in Figure 4.10 and the test procedures include:

1. Fill 50 ml 1:1 diluted HCl solution into the bottle;
2. Weigh about 0.5 g sample (under the natural condition) in the sample hold made of a thin stainless steel plate;
3. Carefully place the holder with the sample to the solution to let the holder float on the solution;
4. Tighten the bottle with its lock and connect the pipe to one of the manometer;
5. Turn on the manometer and zero-set it;
6. Stir the bottle to make the holder sink into the solution (air bubbles may be observed if there is gas release from the sample); and
7. Record the pressure when the value becomes relatively constant.

The released gas from the sample can be calculated by Equation (5).

$$n_g = \frac{V_0 - V_a}{RT} \cdot \frac{\Delta p}{m} \quad (5)$$

where n_g is the released gas (mmol/g), V_0 is the volume of the measurement system including the bottle and the connection pipe (ml), V_a is the volume of acid added into the bottle (ml), Δp is the recorded pressure difference (mbar), m is the mass of the sample (g), R is the gas constant, $R = 83.14 \text{ ml}\cdot\text{mbar}/(\text{mmol}\cdot\text{K})$ and T is the Kelvin temperature in the test room.

Because the stone balls have limited specific surface area due to their larger sizes the consumption of CO_2 should not be significant. Therefore, the gas release measurement was carried out for the improved RCA only. The results are listed in

Table 4.3. If the released gas is due to carbonation the consumption of CO₂ in the curing can be estimated as 31-44 g per kg of the improved RCA. In concrete production the CO₂ value (release of CO₂ including those in raw materials and production processes) is about 230-320 kg/m³, depending on the strength class and the raw materials. The fine sand (0-2 mm) content is about 560-700 kg/m³ or the natural sand (0-8 mm) content is about 800-1000 kg/m³. If the natural sand can be replaced by RCA a reduction of CO₂ value will be about 20-25 kg/m³, implying a reduction of carbon footprint by 8-10%. According to Swedish roadmap for fossil-free competitiveness, one of the ways to the goal of zero emission of CO₂ in 2045 is by carbon capture and utilization (CCU). Although the reduction of 8-10% is not a big number, in addition to the other environmental and economic benefits (saving of natural resource by replacement of RCA), this approach (improvement of fine RCA by bottom ashes) can certainly contribute to the goal.

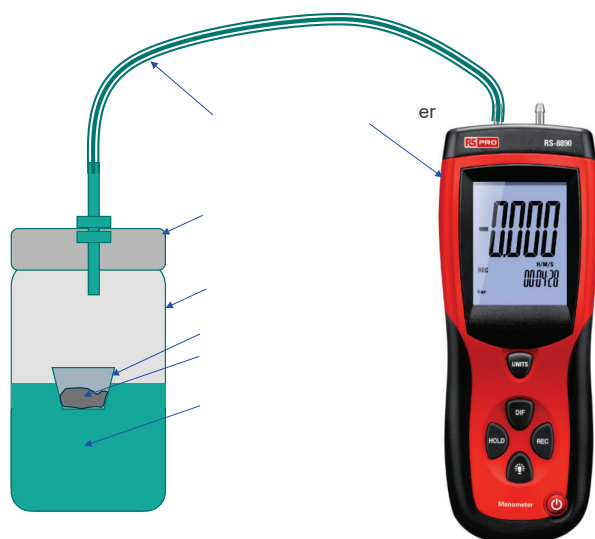


Figure 4.9 – Experimental setup for measurement of gas release.

Table 4.3 – Released gas from the improved RCA.

Sample	R025RCA	S025RCA	GRCA
mmol/g	0.739 ± 0.037	0.998 ± 0.021	0.716 ± 0.116

4.4 LEACHING OF HEAVY METALS

Because of the limited project period we carried out a relatively simple leaching test based on Chinese standard HJ 755-2015 “Solid waste. Extraction procedure for leaching toxicity. Horizontal vibration method” with certain modifications, that is,

1. Dry the samples at 50 °C to constant mass (about 60-72 hours);
2. Weigh 5 grams of sample in a 50 ml centrifugation tube;
3. Fill the tube with 50 ml of demineralized water;
4. Rotate the tube on a rotator at 20 rpm for 4 weeks;
5. Centrifugate the tube on a spinner at 4000 rpm for 30 min; and
6. Pipet 10 ml clear solution with a syringe and inject the solution through a 0.45 µm filter into a 15 ml centrifugation tube for analysis of heavy metal content.

Under the consideration of immobilization mainly due to alkali-activated hydrates, the samples from mixture M1 in manufacturing stone balls as listed in Table 3.1 were used for leaching test. As a trial, only S025 samples with different particle sizes were selected. The chemical analysis was carried out by ALS Scandinavia AB using the analysis method “ME-ICL02”. The results are shown in Table 4.4, where the calculated element concentration in the solution are also listed in the last two rows, assuming 1% elements are leached out from the solid ashes, simply based on the following equation.

$$c_i = \frac{m}{V} \cdot C_i \times 1\% \quad (6)$$

where c_i is the concentration of the i -th element (mg/L), m is the mass of solid sample ($m = 5$ g in this case), V is the volume of the solution ($V = 50$ ml in this case) and C_i is the content of the i -th element in the solid sample. For plain S025, the value of C_i is the average of three samples as shown in Figure 2.3, whilst for sample S025 M1, the GBA content is approximately 15% of the sample mass (assuming a full reaction of the alkali-activator) and thus the value of C_i is 0.15 of the one for plain S025.

It seems that a leaching period of 4 weeks can only leach out a very small portion of the heavy metals, even for the plain GBA. As indicated in the literature [39,40], the reasons could be

1. The heavy metals are in the form of metallic oxides with low solubility in the water; and
2. The bottom ash has already a certain amount of hydration products as shown in Figure 2.4, which have a certain immobilization capacity.

Table 4.4 – Results from the leaching test.

Concentration [mg/L]	Cr	Cu	Ni	Pb	Zn
Plain S025	0.04	0.14	<0.01	<0.02	0.05
S025 M1, 0.5-1 mm	0.02	0.03	<0.01	<0.02	0.03
S025 M1, 1-2 mm	0.02	0.02	<0.01	<0.02	0.02
S025 M1, 2-4 mm	0.01	0.02	0.01	<0.02	0.04
S025 M1, crushed 0.063-0.25 mm	0.03	0.07	<0.01	<0.02	0.01
Element content in plain S025 [mg/kg]	733	5778	344	1587	6350
Element concentration if 1% leached out from plain S025 [mg/L]	0.733	5.78	0.344	1.59	0.635
Element concentration if 1% leached out from S025 M1 [mg/L]	0.11	0.867	0.052	0.238	0.95

5 Conclusions

Through the project a “two-step” technique has been developed to manufacture stone balls using about 8% GBA (according to Table 3.1) and improved fine RCA using about 15% GBA (according to Table 3.3). Based on the results from this project the following conclusions can be drawn:

- The contents of heavy metal elements in bottom ashes from two MSWI plants are similar, independent of particle sizes.
- The current ash discharge system in the incineration plants needs water cooling and storage for sorting off metals before discharging bottom ashes. The potentially hydraulic capacity in the ashes has been released and hydration products were already formed in the ashes under the storage period due to the moist condition and carbonation process.
- The stone balls manufactured from the ground bottom ash and GGBS can improve the workability of fresh concrete and the resistance of hardened concrete to chloride ingress, but with a certain reduction of compressive strength.
- The ground bottom ash together with GGBS and alkali-activator can improve the fine RCA (0-2 mm) to make the RCA sand (0-4 mm) fully applicable in concrete (mortar) without impairing workability and compressive strength.
- Both the stone balls and the improved RCA sand are lighter than the natural aggregates. This will lead to a reduction of concrete weight by about 12% if the natural aggregates are replaced by the green aggregates as developed in this project.
- Curing under a concentrated CO₂ condition may consume 30-40 g CO₂ per kg product (improved fine RCA), leading to a potential reduction of carbon footprint in concrete production by 8-10% if the natural sand can be replaced by the improved fine RCA, in addition to the other environmental and economic benefits (saving of natural resource by replacement of RCA).
- No markedly leached heavy metals can be detected from a simple leaching test after 4 weeks, implying a need for further investigation of long-term leaching behaviour.

As a prospective view, if the bottom ash can be used in concrete as aggregate, it can consume about 170 kg bottom ash per m³ concrete (about 65 kg in stone balls and about 105 kg in the improved sand according to the mix proportions in Table 4.1) or 0.17 tons/m³. According to Swedish statistics [41] the production of concrete is about 6 million m³/year in Sweden. If a half quantity of concrete is produced using the green aggregate as developed in this project, the consumption of bottom ash in concrete will be about 500 000 tons/year – about 70% bottom ash produced in Sweden (700 000 tons/year according to [23]). Therefore, it is worth to further develop the technology to a higher readiness level for industrial applications.

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BOTTOM ASHES FOR GREEN AGGREGATE

Bottenaskor från avfallsförbränning används idag främst för att täcka deponier. Behovet antas minskas under kommande år. Det är därför angeläget att hitta andra områden där aska kan användas på ett säkert och effektivt sätt.

Här har forskare på Chalmers undersökt hur ballastkulor av slaggrus kan tillverkas med koldioxid som härdnings- och reaktionsmedium. Koldioxid binds då in i ballasten vilket minskar betongens totala koldioxidavtryck när ballasten ersätter grus och sand i betongen. Resultaten visar också att tungmetaller inte lakas ut ur ballasten.

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