UNIVERSIDADE DA BEIRA INTERIOR
Engenharia

Synthesis and Characterisation of CO_2 Activated Binders and Concretes using Industrial Wastes for Precast Buildings Applications

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Tese para obtenção do Grau de Doutor em

Engenharia Civil

(3º ciclo de estudos)

Orientador: Prof. Doutor João Paulo de Castro Gomes

Covilhã, Fevereiro de 2020

This thesis was partially supported by the Doctoral Incentive Grant BID/ICI-FE/Santander Universidades-UBI/2017 financed by the Santander-Totta bank and the University of Beira Interior.

This thesis was also partially financed by Portuguese national funds through FCT – Foundation for Science and Technology, IP, within the research unit C-MADE, Centre of Materials and Building Technologies (CIVE-Central Covilhã-4082), University of Beira Interior, Portugal.

This thesis was supported with Portuguese national funds by FCT - Foundation for Science and Technology within the UID/ECI/04082/2013 project.

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Dedication

To Luiz, my son.

Acknowledgements

First, I would like to thank Luiz, my son: you do not know yet, but you are the one who motivates me the most and makes me keep going forward, you are the meaning of every single step I take on my journey. I would also like to thank your mom, Amanda, who is in the field, every day, covering my role and providing you the best and the purest love.
Secondly, I would like to thank my two moms, Ivany and Ailda (in peace) who have devoted a great part of their lives in order to provide me the best education, food, and directions on this great labyrinth which is life. God, Allah, Energy or whatever it is named, comes along in all positions, with all my respect and belief to all religions, traditions, and creeds as long as there is no harm to other living beings.
Thirdly, I would put together my family and friends, highlighting my siblings Jana, Júlia, Maria, Eduardo, Bomani, Rudá, Luca, Cauê and Tauá, my father Luiz, my long-time friends from Lua Nova to Módulo, and the genius I met in Budapest.
I also thank every single person who has welcomed me, supported or was part of this adventure here in Portugal, highlighting my supervisor João, my colleagues Gabriel, Naim, Imed, Hakim, Tarek, and Marcia, all professors, staff, technicians and, especially, the cleaning ladies with the best morning smiles ever, my Jiu-Jitsu mates Romário, Thaís, Bruno and Marcão, and my friends Ana and Sofia.

Resumo

Esta investigação foi concretizada no âmbito da sintetização e caracterização de aglomerados compostos por escória de aço da Siderurgia Nacional de Maia e Seixal, Portugal, e ativados por carbonatação acelerada. Esta tese de doutoramento apresenta um extenso estudo acerca desta tecnologia. Inicia-se com uma reflexão sobre o estado da arte, evidenciando os estudos mais relevantes nesta temática, além de identificar de forma sistemática os pontos a investigar e que serão, consequentemente, abordados também nesta tese.

As propriedades da escória de aço da Siderurgia Nacional foram caracterizadas através de análises e ensaios para determinar a densidade e espessura; análise de microscópio eletrónico de varredura para caracterizar os elementos; e difração de raio x para identificar as fases mineralógicas do material.

O processo de preparação da amostra é discutido e explicado detalhadamente, indicando as etapas de secagem, moagem, separação granulométrica, mistura e compactação. A realização destas etapas, além de garantir a concordância e confiabilidade dos resultados, influencia diretamente as propriedades do produto final e possibilita que, ao alterar cada processo, o produto final seja aprimorado e os processos ótimos sejam parametrizados. O estudo sobre a utilização de aditivos no processo de endurecimento da escória de aço através da cura em dióxido de carbono (CO_2), também é exposto e comparado a estudos relevantes em áreas correlacionadas.

Um amplo estudo, referente às condições de cura por carbonatação acelerada é evidenciado, indicando os parâmetros que são controlados, e as respetivas influências nos resultados finais devido à manipulação destes mesmos. Os parâmetros investigados foram: temperatura, pressão parcial do CO_2, tempo de cura e humidade; os respetivos efeitos foram sistematizados. Para além da cura em CO_2, foi desenvolvida uma análise do efeito de métodos de curas complementares, correlacionadas com o ganho de resistência a compressão dos produtos finais. As amostras, após se ativarem por carbonatação, foram submetidas, por um período controlado, ao forno, câmara húmida, saco plástico e submersão em água; os efeitos desta cura alternativa foram expostos e discutidos.

O aglomerado composto por escória de aço e ativado por cura em CO_2 teve a sua microestrutura caracterizada através de análises microscópio eletrónico de varredura, análise de difração de raio x mineralógica e análise termogravimétrica, possibilitando a identificação dos produtos gerados, consequentes da carbonatação da escória de aço.

A investigação utilizou o cimento Portland, submetido a estas condições, para realização das análises, tendo efetuado a sua caracterização. O estudo expõe as condições ótimas de ativação.

Palavras-chave

Escória de Aço, Ativação com Dióxido de Carbono, Materiais de Construção Sustentáveis, Materiais de Construção Livres de Clínquer.

Resumo Alargado

1. Enquadramento

Este trabalho apresenta a síntese e caracterização de aglomerados compostos por escória de aço da Siderurgia Nacional de Maia e Seixal, Portugal, ativados por carbonatação acelerada. O trabalho foi desenvolvido no C-MADE, Centre of Materials and Building Technologies, entre 2016 e 2019, que deu lugar a uma patente de invenção nacional 110895. O presente estudo surge na sequência desse trabalho de investigação e integra-se no âmbito da Bolsa de Doutoramento BID/ICI-FE/SantanderUniversidades-UBI/2017 financiada pelo Santander-Totta e pela Universidade da Beira Interior.

2. Descrição do Problema

O aquecimento global é causado pelo acumular de produção de gases da estufa (GEE); portanto, encontrar métodos eficientes para reduzir sua produção, implementando sistemas de captura e armazenamento, é fundamental. Os GEEs incluem dióxido de carbono (CO_2), metano (CH_4), óxido nitroso (N_2O), hidrofluorcarbonos (HFCs), perfluorcarbonos (PFCs) e hexafluorocarboneto de enxofre (F6C). Atualmente, os GEEs emitidos abundantemente são CO_2 (56%) e CH_4 (18%) [1].
O aquecimento global ultrapassou limites graves em 2015, principalmente devido ao alto teor de dióxido de carbono (CO_2) na atmosfera [2]. Emissões de CO_2 de 4,45 mil milhões de toneladas de CO_2-equivalentes em 2015 [3] de um espectro de processos industriais impõem impactos negativos ao meio ambiente e à saúde humana.
Em relação à produção de CO_2, as usinas a combustível fóssil são as maiores fontes (40% do total de emissões de CO_2). Outras fontes de CO_2 surgem do transporte e da indústria em geral [3]. Em relação ao setor de construção civil, a indústria de cimento Portland é responsável por emitir 15% das emissões indiretas de CO_2 provenientes do uso não energético; além disso, o processo de produção consome uma enorme quantidade de energia [4].
Os resíduos da atividade económica e dos domicílios europeus produziram 2,5 bilhões de toneladas em 2014. A maior parte desses resíduos foi despejada em aterros sanitários, resultando em potenciais problemas de saúde pública a longo prazo, contaminação do solo e da água [5]. Este comportamento de gestão de resíduos resulta no acumular de grande quantidade de resíduos minerais depositados em campos que levam à poluição ambiental e impactos paisagísticos sérios, que afetam a qualidade de vida da população local. Medidas preventivas envolvem, normalmente, o uso de barragens de terra/rocha ou lagoas para armazenar resíduos. Infelizmente, o potencial colapso destas estruturas pode ter sérios impactos no meio ambiente e na saúde e segurança humanas [6]. Na indústria siderúrgica a

escória de aço é o principal subproduto, produzido em larga escala. O processo de fabricação de aço usa três fornos diferentes: o forno básico de oxigênio (BOF) é usado no primeiro refinamento do processo siderúrgico com ferro fundido, sucatas de aço e calcário ou dolomita como catalizador; o forno de arco elétrico (EAF) tem um processo similar de refino de aço, mas usa arcos elétricos de alta potência para produzir aço de alta qualidade a partir de sucata de aço reciclada. Após ser refinado pelo BOF ou EAF, o aço pode ser refinado novamente através de uma operação secundária de fabricação de aço, que visa obter uma composição química específica. Esta operação secundária usa o forno panela que é semelhante ao EAF e tem escória de panela como subproduto [7]. A produção anual de escória de aço no mundo é de cerca de 130 milhões de toneladas, que são principalmente escórias de Forno Elétrico a Arco (EAF) e Forno Básico de Oxigênio (BOF) [8]. A maior parte dessa produção é descartada em aterros sanitários; a escória é também usada como agregados para diferentes fins de construção, tais como betão pronto, betão asfáltico, bases e superfícies de estradas e preenchimentos [9].

3. Argumento de Tese

Esta tese propõe uma nova abordagem referente aos aglomerados compostos por escória de aço, e ativados por carbonatação acelerada, no que se refere a preparação do produto – demonstrando as condições de endurecimento desempenhadas, de modo a evidenciar características e propriedades deste material.
O aglutinante CO_2 ativado consiste em escória de aço e outros resíduos que são ricos em cálcio e sílica ativada numa atmosfera com CO_2 capturado. Assim, é possível reduzir o consumo de cimento Portland, reduzindo também as emissões de CO_2 e a energia incorporada e permanentemente armazenando CO_2 através da carbonatação que ativará o aglomerante. Num futuro próximo, estes e outros materiais de construção pré-fabricados “amigos do ambiente” poderão estar presentes em projetados de engenharia.

4. Principais Objetivos

Assim, este trabalho tem como objetivos:

- Estudar a composição química da escória de aço portuguesa;
- Estudar as condições de exposição, como pressão parcial de CO_2, temperatura e fonte de CO_2;
- Estudar as propriedades dos resíduos, como tamanho de partícula e área de superfície;
- Estudar as condições de cura de CO_2, como pressão parcial de CO_2, temperatura da câmara e duração da cura;
- Estudar a capacidade e eficiência de absorção de CO_2;

- Determinar a composição química por espectrometria de dispersão de energia (SEM/EDS) e difração de raios X (XRD);
- Estudar a compatibilidade destes resíduos com os principais resíduos usados para melhorar as condições de carbonatação;
- Determinar possíveis adições que estarão nas misturas de encadernação;
- Determinar os procedimentos de carbonatação a serem seguidos com as misturas de ligantes;
- Determinar as condições da câmara a serem aplicadas com as misturas de ligantes;
- Determinar a composição das misturas e a razão de massa de cada conteúdo;
- Testar todas as misturas com todos os diferentes procedimentos definidos;
- Analisar a microestrutura dos ligantes;
- Analisar os resultados da análise termogravimétrica (TGA);
- Determinar a resistência à compressão dos ligantes;
- Determinar a composição química por análises (SEM/EDS) e (XRD).

5. Metodologia

Primeiramente, foi realizada uma introdução, evidenciando o estudo, a sua legitimidade e relevância. Depois, o estado da arte foi apurado para evidenciar estudos anteriores a esta pesquisa. Em seguida, procedeu-se a um programa experimental, evidenciando em detalhe o trabalho a ser realizado. Os materiais e métodos foram caracterizados, onde as condições de carbonatação foram destacadas e os dados foram analisados e interpretados, discutindo os resultados da investigação. Por fim, a conclusão evidenciou as descobertas mais relevantes e sugeriu a realização de pesquisas complementares.

6. Principais Contribuições

6.1. Revisão Bibliográfica dos Materiais Feitos com Escória do Aço Ativados com Dióxido de Carbono

Este trabalho discute o estado-da-arte dos materiais à base de escória de aço ativado por dióxido de carbono (CO_2), evidenciando pesquisas anteriores conduzidas na área, destacando os principais resultados, descobertas e oportunidades para futuras pesquisas.

6.2. Caracterização do Aglomerante

O objetivo é estudar um novo aglomerante, à base de escória de forno de acro elétrico (EAF) ativado por CO_2, analisando a influência da preparação da amostra, condições de carbonatação,

aditivos e cura complementar no desenvolvimento da resistência à compressão do aglomerante. Pretende-se analisar e caracterizar ligantes à base de escória de EAF ativados por CO_2 com potencial como substituto de ligante à base de cimento Portland para aplicações de construção pré-moldada. O aglutinante ativado por CO_2 consiste em escória de EAF que é rica em cálcio e ativada sob uma atmosfera controlada rica em CO_2.

6.3. Análise da Preparação das Amostras

A investigação apresenta a análise da preparação das amostras de uma escória de aciaria da Indústria Siderúrgica Nacional, onde a mesma foi colocada no forno a 60 ºC por 24 h para secar. Este processo foi realizado para melhorar a fase de moagem, reduzindo a possibilidade de aglutinação de pós finos que poderiam retardar o processo de moagem, e solicitar uma fase extra antes da separação do tamanho de grãos, uma vez que os grãos aglutinados não passariam sobre a peneira corretamente.

Após a secagem, a escória EAF foi primeiro submetida a um moinho triturador para ser moída num tamanho pequeno. Este processo de moagem teve um consumo de energia de 12 kWh por tonelada de escória de aço triturada. Depois de ser moído, a fim de pulverizar o pó de escória EAF em tamanhos de grão inferiores a 45 µm e 125 µm, o pó de escória EAF foi submetido a um moinho de bolas. O processo de pulverização teve um consumo de energia de 12,5 kWh e 37,5 kWh por tonelada de pó de escória de aço mais grosso e fino, respetivamente.

Após a pulverização, cada pó de escória de EAF foi peneirado por uma peneira de 45 µm e peneira de 125 µm, a fim de assegurar que nenhum tamanho de partícula acima da dimensão máxima desejada estivesse presente no lote.

As escórias EAF, Slag 45 e Slag 125, foram misturadas com três diferentes proporções de água para sólido, sempre calculadas em peso. Cada mistura foi preparada com 100 g de pó de escória de EAF mais água, dependendo da razão específica de água para sólido. Para cada mistura, três amostras foram posteriormente moldadas e compactadas. A relação mássica água/sólido utilizada foi de 10,0%, 12,5% e 15,0%.

Após este processo, a mistura foi vertida para um molde cilíndrico de 20 mm de diâmetro e 60 mm de altura e compactado por uma máquina de ensaios mecânicos electro-hidráulicos de 3.000 kN (Máquina de compressão ADR Touch 3000 BS EN com leitura digital e autocentrantes) de acordo com a EN 196-1 sob três diferentes pressões de compactação de 10, 20 e 30 MPa. Amostras frescas tinham 20 mm de diâmetro e 40 ± 05 mm de altura.

6.4. Verificação do Impacto das Variações das Condições de Cura no Aglomerante

Verificou-se o impacto das variações das condições de cura no aglomerante, onde as amostras moldadas frescas foram colocadas na câmara de carbonatação que estava dentro de um forno. O forno já estava a trabalhar com a temperatura desejável estável. Quatro diferentes

temperaturas foram estudadas, 40 ºC, 50 ºC, 60 ºC e 70 ºC, a fim de encontrar a temperatura ideal que aumentaria a ativação do CO_2 para alcançar um maior desenvolvimento da resistência à compressão.

A câmara de carbonatação estava à temperatura ambiente (17,5 ± 0,2 ºC) e teve seu crescimento de temperatura dentro da câmara medida (HygroLog HL-NT3-DP) para cada temperatura estudada antes de colocá-la no forno registando os dados em períodos de cinco minutos, para registar o balanço de temperatura entre a câmara e o forno. A temperatura do forno foi semelhante à temperatura no interior da câmara após 40, 50, 55 e 60 min quando o forno estava a 40 ºC, 50 ºC, 60 ºC e 70 ºC respetivamente.

Depois de colocar as amostras dentro da câmara, travando-a e colocando a câmara dentro do forno, o CO_2 foi injetado dentro da câmara até 0,5 bar de pressão parcial. Em seguida, uma válvula de topo foi aberta para liberar o ar atmosférico da câmara à atmosfera e, em seguida, o CO_2 foi injetado novamente para atingir a pressão parcial experimental. Três diferentes pressões parciais de CO_2 foram aplicadas durante o trabalho de pesquisa 0,5 bar, 1,5 bar e 2,5 bar. O fluxo de CO_2 permaneceu fixo na pressão parcial desejável para reabastecer o CO_2 consumido da amostra sob carbonatação. Cada teste tinha apenas três amostras dentro da câmara de carbonatação ao mesmo tempo.

Após a injeção do CO_2, as amostras foram submetidas à carbonatação por oito diferentes períodos estabelecidos, 0, 5, 2, 4, 8, 12, 24, 48 e 72h. Após a carbonatação, as amostras foram retiradas da câmara para secar em estufa por 20 horas a 40 ºC de temperatura e depois submetidas a várias análises diferentes logo após o período de secagem.

6.5. Classificação de Potenciais Aditivos Utilizados na Carbonatação dos Aglomerantes Feitos de Escória do Aço

Potenciais aditivos foram verificados e classificado no âmbito da carbonatação dos aglomerantes feitos de escória do aço. Uma vez que a abordagem de carbonatação como método de cura é nova, não há muitas pesquisas conduzidas relativamente à influência e utilização aditiva para melhorar a reação em si. Com o objetivo de aumentar o captação de dióxido de carbono no betão, Haselbach e Thomle investigaram a influência da adição de bicarbonato de sódio em diferentes concentrações para simular a água dos rios e avaliar se a carbonatação aumentaria, em comparação com uma carbonatação média exposta apenas ao ar. Estes autores observaram que, aumentando a concentração de bicarbonato de sódio, o pH das amostras de betão diminuiu mais rapidamente, o que pode representar um aumento na taxa de carbonatação [10]. Numa abordagem semelhante, investigadores da Universidade da Coreia pesquisaram a influência do cloreto de sódio (NaCl) na carbonatação do betão, variando a concentração de NaCl na água avaliando também o comportamento do pH durante a experiência. A pesquisa evidenciou que a formação de carbonatos de cálcio aumentou para 18,4%, enquanto a formação de CSH diminuiu até 33,0%, revelando que a carbonatação aumenta

pela utilização de NaCl [11]. No entanto, estes estudos analisam a utilização de aditivo para amostras carbonatadas com betão endurecido. Nesta tese, a utilização de aditivo foi conduzida para entender a influência de potenciais aditivos para melhorar a cura de carbonatação de ligantes à base de escória de aciaria. Além de utilizar cloreto de sódio e bicarbonato de sódio, o etanol, devido ao seu teor de carbono e alta volatilidade, foi utilizado como aditivo de modificação da água. Além disso, os resíduos de vidro têm sido utilizados como substituto da escória de aço para avaliar se o seu alto teor de sílica aumentaria a reação.

Três diferentes aditivos foram testados parcialmente substituídos ou dissolvidos em água. A modificação e substituição da água foi feita antes da mistura com a escória EAF. Etanol, cloreto de sódio (NaCl) e bicarbonato de sódio ($NaHCO_3$) foram usados para substituir parcialmente ou modificar a composição da água. O etanol (96%) substituiu 10%, 20% e 30% de água, NaCl foi dissolvido em água nas concentrações de 10 g/L, 20 g/L e 30 g/L, enquanto $NaHCO_3$ foi dissolvido em água nas concentrações de 100 mg/L, 200 mg/L e 300 mg/L. Todas as amostras que possuíam aditivos de modificação de água foram preparadas apenas com Slag 45, com 10% de água para sólidos, 30 MPa de pressão de compactação e submetidas a carbonatação a 60 ^oC, com pressão parcial de CO_2 de 0,5 bar por 24h.

Um aditivo foi testado substituindo parcialmente a escória EAF. A substituição foi feita antes de misturar a escória EAF com água. Os resíduos de vidro recolhidos no restaurante local da Covilhã foram moídos por uma trituradora e substituídos em 5%, 10% e 15%. As amostras que apresentaram aditivo de substituição de escória EAF foram preparadas apenas com Slag 45, com 10% de água para sólidos, 30 MPa de pressão de compactação e submetidas a carbonatação a 60 ^oC, com pressão parcial de CO_2 de 0,5 bar por 24 h.

6.6. Identificação dos Resultados de Uma Cura Complementar no Endurecimento dos Materiais

Ficou demonstrada a eficiência da realização de uma cura complementar no endurecimento dos materiais feitos de escória de aço. O grau de hidratação e consequentemente o desenvolvimento da resistência à compressão de aglomerantes à base de cimento Portland e materiais de construção após 24h de cura ainda abaixo de 50%, atingindo 80% somente após pelo menos sete dias (168 h) de cura, geralmente por exposição ao ar ambiente (65,66). O estudo de cura complementar deste trabalho deve analisar se a escória EAF após 24h de carbonatação ainda pode desenvolver qualquer resistência à compressão, devido a diferentes tipos de métodos de cura, ou se há alguma implicação numa cura preliminar antes da ativação do dióxido de carbono. Este trabalho apresenta uma análise sobre quatro diferentes métodos de cura complementares: cura de água, cura em sala húmida, cura de saco plástico, cura em forno. Uma condição extra foi analisada sem qualquer etapa complementar de cura ou secagem para avaliar se a etapa de secagem teve alguma influência no desenvolvimento da resistência à compressão.

7. Estado da Arte

7.1. Materiais à Base de Escória de Aço Obtidos por Cura / Ativação de CO_2

Existem numerosos estudos sobre a carbonatação de materiais à base de cimento Portland, como a revisão, onde Ashraf resumiu as informações relevantes desses recursos de carbonatação e destacou as áreas onde outras investigações poderiam ser feitas [12]. Além dessa abordagem geral, Jang e colaboradores, focou a pesquisa na captação de CO_2 [13], Zhang e colaboradores, analisaram a aplicação da carbonatação pelo seu mecanismo de cura, propriedades alcançadas e viabilidade [14].

A escória de aço utilizada como alternativa à matéria-prima reciclada ativada por CO_2 está a ser estudada recentemente e considerada uma solução para armazenar CO_2, reduzir as emissões de GEE, bem como reciclar e valorizar os resíduos da indústria siderúrgica. Um desafio nos materiais curados/ativados com dióxido de carbono à base de escória de aço está relacionado com a variedade da sua composição química, que depende da especificação de fabricação do aço. Diferentes bancos de escória têm uma composição e estrutura química diferentes, dificultando a modelagem e a compreensão da reação de carbonatação [15].

7.2. Composição da Escória de Aço e Reatividade de Carbonatação

A escória de aço é o principal subproduto da fabricação de aço e muitas vezes despejada em aterros sanitários. Na Europa, a atividade de construção de estradas usa uma quantidade expressiva de escória como agregados. No ano de 2012, quase metade da escória produzida foi utilizada. No entanto, existe, ainda, uma grande quantidade de escória que não foi reutilizada nem submetida a um processo de reciclagem [16].

A composição química da escória de aço depende do processo siderúrgico, que também é um fator importante para sua reatividade ao CO_2. A escória de forno de oxigénio básico (BOF) tem como componentes principais cálcio, ferro e óxidos de sílica. O óxido de ferro (FeO/Fe_2O_3) pode ser de até 38%, a sílica (SiO_2) varia de 7 a 15% e o óxido de cálcio (CaO) é o composto mais alto, variando de 36 a 60% [17].

A escória de forno a arco elétrico tem composição semelhante à escória de forno de base de oxigénio devido a semelhanças nos processos de produção, no entanto, como usa sucatas de aço recicladas, a composição química da escória de forno a arco elétrico também depende das propriedades da sucata de aço. O teor de ferro pode ser de até 40%, SiO_2 é cerca de 16% e o CaO não é o composto mais alto, como na escória de forno de oxigênio básico, variando de 23 a 38% [18,19].

Como o processo de fornos em panela é secundário e com algumas ligas, esta escória difere mais do forno de base de oxigénio do que do forno de arco elétrico, dependendo do tipo de aço produzido. O teor de FeO é muito menor, sendo inferior a 5%, SiO_2 pode ser quase 20% e o CaO

também é maior, variando de 42 a 57% [20]. A Tabela 1 mostra a composição química das escórias de aço de diferentes estudos que confirmam a grande variabilidade de sua composição.

Table 1 - Steel slag: types and oxide compositions (%)

Referência	Tipo	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3
[21]	BOFS	47.9	12.2	1.2	0.8	—
[22]		61.21	24.92	1.83	4.89	3.04
[23]		36.4-45.8	10.7-15.2	1-3.4	4.1-7.8	—
[24]		47.5	11.8	2.0	6.3	22.6
[25]		39.08	12.47	6.87	10.57	19.48
[26]		42.42	11.04	1.61	7.19	27.37
[27]		39.3	7.8	0.98	8.56	38.06
[18]		45.0	11.1	1.9	9.6	10.9
[17]		47.7	13.3	3.0	6.4	24.4
[28]		23.9	20.75	0.84	3.775	—
[19]	EAFS	24.4	15.4	12.2	2.9	—
[25]		35.23	9.41	10.78	9.77	24.22
[29]		23.9	15.3	7.4	5.1	—
[18]		38.8	14.1	6.7	3.9	20.3
[30]		35.7	17.5	6.3	6.5	26.4
[31]	GGBS	65.04	20.71	4.83	1.03	2.77
[32]		39.80	36.00	10.53	7.93	0.67
[33]		42.5	31.9	13	4.81	0.34
[34]	LFS	65.23	12.35	16.55	3.96	0.79
		57.55	6.21	23.17	5.04	3.55
[35]		49.6	14.7	25.6	7.9	0.22
[36]		49.5	19.59	12.3	7.4	0.9
[20]		50.5-57.5	12.6-19.8	4.3-18.6	7.5-11.9	1.6-3.3
[18]		42.5	14.2	22.9	12.6	1.1
[37]	Steel Slag	51.05	25.80	2.31	9.32	0.72
[38]		42.42	11.04	1.61	7.19	27.37
[39]		54.30	17.70	6.40	9.20	3.00
[40]		45-60	10-15	1-5	3-13	3-9
[25]	Mix of EAF and BOF slags	39.08	12.47	6.87	10.57	19.48

[a] O intervalo de valores é compilado com base nos dados da composição química de diferentes fontes

— = dados não disponíveis

A escória de aço não possui uma boa propriedade hidráulica, devido ao seu teor de SiO2 é amorfa e a pequena quantidade de silicatos de tri-cálcio é apresentada em suas fases mineralógicas [41]. Portanto, o potencial de ligação e a contribuição da escória de aço na resistência à compressão em sistemas de cimento Portland não são significativos para métodos convencionais de hidratação/humidade. Outra desvantagem da substituição de escória de aço e uso no cimento tradicional é sua expansão desordenada e instabilidade de volume ao longo do tempo causada pelo alto teor de CaO/MgO livre [42]. No entanto, esta expansão pode ser evitada ou reduzida pela carbonatação da escória de aço devido ao consumo de calcário livre, a principal fase expansiva [43].
A escória de aço possui alta reatividade de carbonatação devido ao seu teor de CaO/MgO livre, tornando a escória uma boa matéria-prima para materiais de construção ativados por carbonatação [44]. Associado com o CaO/MgO livre, o silicato de cálcio hidráulico (Ca3SiO5 (C3S), ß-Ca_2SiO_4 (C_2S)), silicato de cálcio não hidráulico (γ-C_2S, $CaSiO_3$ (CS)), e Portlandite (produtos de hidratação de CaO livre ou silicato de cálcio), são, também, componentes reativos para a carbonatação de escória de aciaria [22]. Estes componentes reativos proporcionam a formação de carbonatos de cálcio/magnésio e hidratos de silicato de cálcio, que são as principais fases responsáveis pela capacidade de ligação e desenvolvimento da resistência à compressão [45].

7.3. Materiais com Ativação de Dióxido de Carbono

A carbonatação é uma reação química entre diferentes silicatos e CO_2 que produz principalmente carbonatos com propriedades de ligação. A carbonatação também contribui para melhorar as propriedades mecânicas e a durabilidade dos materiais enquanto armazena e usa CO_2 como fonte para a reação [13]. Em geral, os materiais podem ser carbonatados com diferentes propósitos, como armazenamento de CO_2, melhoria da propriedade de betão e desenvolvimento de aglutinante ativado por dióxido de carbono [12]. Para materiais ativados com dióxido de carbono, a carbonatação também tem o papel de endurecimento.

7.3.1. Compostos Principalmente Reativos

O processo de carbonatação da escória de aciaria inclui três reações principais: hidratação e dissolução de CO_2, lixiviação de Ca^{2+} e Mg^{2+} e precipitação de carbonatos. Em primeiro lugar, o CO_2 difunde-se na pasta e dissolve-se na solução de poros para formar o ácido carbónico (H_2CO_3).
Então, a reação é seguida por ionização de H_2CO_3 para iões HCO^{3-}, CO_3^{2-} e H^+ como pode ser visto na Eq. (1) [33].

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \quad (1)$$

Subsequentemente, a reação de CO_3^{2-} com iões Ca^{2+} e Mg^{2+} lixiviados da escória de aço resulta na formação e precipitação de carbonatos contendo cálcio e magnésio, como mostrado na Eq. (2) e (3) [46].

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (2)$$
$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \quad (3)$$

Na presença de Mg^{2+}, calcita magnesiana com incorporação de Mg^{2+} no $CaCO_3$ pode ser formada em pastas carbonatadas, mas é difícil de ser distinguida com DRX devido a padrões sobrepostos de calcita magnesiana e calcita [26].
A escória misturada com água num ambiente de dióxido de carbono representa a carbonatação que ocorre para os materiais ativados/curados com dióxido de carbono, onde diferentes silicatos de cálcio, como Alite (C3S), Belite (γ/ß-C_2S), são carbonatadas e hidratadas ao mesmo tempo. Tal pode ser descrito através da Eq. (4) e (5), onde carbonatos de cálcio e hidratos de silicato de cálcio são formados como os principais produtos de reação da carbonatação da escória de aço [47].

$$2(3CaO \times SiO_2) + 3CO_2 + 3H_2O \rightarrow 3CaO \times 2SiO_2 \times 3H_2O + 3CaCO_3 \quad (4)$$
$$2(2CaO \times SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO \times 2SiO_2 \times 3H_2O + CaCO_3 \quad (5)$$

Depois de hidratados, alguns produtos podem ser carbonatados também. Tal acontece com o hidróxido de cálcio e os hidratos de silicato de cálcio. A carbonatação do hidróxido de cálcio ocorre com base em três reações; a reação principal é expressa como na Eq. (6)[13].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (6)$$

A carbonatação dos hidratos de cálcio (CSH) inicia-se após o consumo do hidróxido de cálcio durante a reação. Esta reação não está completamente definida e pode ser expressa da seguinte forma na Eq. (7) [48].

$$xCaO \cdot ySiO_2 \cdot zH_2O + xCO_2 \rightarrow xCaCO_3 + y(SiO_2) \cdot H_2O) + (z - yt)\, H_2O \quad (7)$$

Pesquisas relacionadas com diferentes resíduos reativos a CO_2 descobriram que a carbonatação pode acontecer também com o ferro (Fe) em um ambiente aquoso e pode ser visto na Eq. (8) [21].

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \quad (8)$$

7.3.2. Absorção de Dióxido de Carbono pela Ativação de Escória de Aço

A capacidade de absorção de CO_2 de um material pode ser calculada com uma fórmula teórica [49] onde a condição de exposição e a constante de carbonatação da composição do material devem ser determinadas. Então, é possível prever a profundidade de carbonatação e calcular o volume do betão carbonatado. Finalmente, este volume deve ser convertido na quantidade de absorção de CO_2 [50]. Estudos estimam que até 52% da absorção de CO_2 pela carbonatação de resíduos ricos em cálcio [51]. A capacidade teórica de captação também pode ser prevista com base na composição química do material, através da fórmula de Steinour na Eq. (9) [13] ou a fórmula de Huntzinger na Eq. (10) [52].

$$CO_2 \text{ uptake } (\%) = 0.785(CaO - 0.7SO_3) + 1.09Na_2O + 0.93K_2O \quad (9)$$

$$CO_2 \text{ uptake } (\%) = 0.785(CaO - 0.56Ca(CO_3) - 0.7SO_3) + 1.091MgO + 0.71Na_2O + 0.468K_2O \quad (10)$$

Como as escórias têm uma fase mineralógica não linear e uma composição química, a capacidade máxima de absorção pode não ser calculada ou facilmente prevista. A capacidade real de absorção dependerá da finura do pó da escória e das condições de carbonatação. Além disso, a escória de aço pode atingir até 75% da sua absorção máxima teórica com base na sua massa [53].

Métodos experimentais podem encontrar o real consumo de CO_2 através de diferentes análises e cálculos. O ganho de massa e a curva de massa são comuns. No método de ganho de massa, é possível quantificar a quantidade de CO_2 absorvida pelo material, comparando a diferença entre a massa antes e depois da carbonatação. No método da curva, há uma vantagem ao medir a absorção de CO_2 do início ao fim do processo de carbonatação e utilizá-lo como uma ferramenta para avaliar a consistência dos resultados do método de ganho de massa. As equações do ganho de massa e da curva de massa são respetivamente (11) e (12): [54]

$$CO_2 \text{ absorção } (\%) = (\text{Massa final} + \text{Massa de água perdida} - \text{Massa inicial})/\text{Massa da escória seca} \quad (11)$$

$$CO_2 \text{ absorção } (\%) = (\text{Massa residual} - \text{Massa residual secundária})/\text{Massa da escória} \quad (12)$$

Outro método experimental é o analisador de CO_2 que mede a absorção de CO_2, comparando a diferença no conteúdo de carbono (CC) entre uma amostra carbonatada e não carbonatada, como visto pela seguinte equação (13): [22]

$$\text{Absorção de } CO_2 \ (\%) = (\text{CC em escória carbonatada} - \text{CC em escória não carbonatada}) / \text{Massa de escória seca} \quad (13)$$

Outro método de captação está relacionado com a queda de pressão na câmara de carbonatação, com o volume da câmara e a temperatura que é demonstrada na Eq. (14).
No entanto, como a pressão varia com a temperatura, este método deve ser cuidadosamente calculado: [33]

nCO_2 = (Queda de pressão x Volume da câmara)/ Constante universal dos gases x Temperatura (14)

A constante universal dos gases é $8,31x10^{-3}$ L x bar / K x mol.
Os investigadores também usam métodos indiretos para analisar a eficiência da carbonatação nas amostras, como análise termogravimétrica (TGA) e difração de raios-X (XRD). Esta revela os produtos originados da reação de carbonatação pela análise das curvas de perda de massa e os diagramas de fases mineralógicas [32].

7.3.3. Condições de Captação de CO_2 e Procedimentos para Ativação de Escória de Aciaria

As condições de captação de CO_2 são importantes para serem controladas e compreendidas, pois afetam a cinética da reação de carbonatação e têm forte influência no desenvolvimento das propriedades do material. O teor de água da mistura é um parâmetro crítico porque influencia a reatividade. Além disso, a difusividade do dióxido de carbono através da amostra depende da água livre presente nos poros da matriz [55]. A proporção ótima de água para sólido para alcançar maior grau de carbonatação depende da finura da escória [31]. A relação água para escória utilizada em diferentes estudos de pesquisa é mostrada na Tabela 2.

Table 2 - Carbonation conditions of recent researches on carbon dioxide activation.

Referência	Material	Relação entre Água e Sólidos	Número Blaine (m^2/kg)	Concen-tração de CO_2 (%)	Pressão (MPa)	Duração Carbona-tação (h)	Pressão de Compactação (MPa)
[22]	Aglome-rante	0.15	316		0.15	2-24	16
[37]	Aglome-rante	0.125		100	0.3	1	0.5
[34]	Aglome-rante	0.1	247 - 318		0.15	24	12.5
[15]	Bloco de alvenaria	0.18 -0.2	239		0.15	24	12
[25]	Painel de escória	0.08	178		0.15	2 - 24	12.5
	Painel de escória	0.08	178 - 239		0.15	2 - 24	12.5
[38]	Aglome-rante	0.4		99.9	0.15	24 - 336	
[39]	Aglome-rante	0.5	359	5		168 - 672	

Ao controlar a humidade relativa, é alcançada uma ativação mais eficiente. Na carbonatação geral, a condição ótima foi encontrada quando a humidade relativa estava entre 50-70% para uma reação efetiva [13]. Além de melhorar a difusão de CO_2, a humidade provoca maior hidratação das fases não reagidas [56]. No entanto, os investigadores que desenvolveram materiais ativados com dióxido de carbono não controlaram esse parâmetro durante as experiências.

A finura da escória tem forte influência na ativação do dióxido de carbono quando o tamanho da partícula é menor, a área superficial é maior, favorecendo a reatividade da escória e as condições de carbonatação [57]. A fineza Blaine de estudos anteriores também é mostrada na Tabela 2.

A eficiência de ativação do dióxido de carbono tem alta dependência da concentração de CO_2, esta pode ser confirmada pelo desenvolvimento da resistência à compressão para diferentes concentrações. Alguns autores descobriram que 20% da concentração de CO_2, que simula o gás residual industrial, é responsável pelo desenvolvimento da resistência à compressão ser três vezes menor em comparação com um gás de 99,9% de concentração de CO_2, ambos com seis horas de duração de carbonatação [58]. Portanto, uma fonte de CO_2 altamente concentrado aumenta a taxa de carbonatação pela concentração de CO_2 no ambiente. Além da concentração, a pressão parcial de CO_2 tem influência na sua difusividade, uma vez que a matriz do material é carbonatada a baixa pressão, a precipitação do carbonato de cálcio diminui a porosidade, inibindo a difusividade do CO_2. Entretanto, um pouco de CO_2 é difundido na matriz a alta pressão antes dos poros serem fechados por carbonato de cálcio [59]. Para ligantes ativados por CO_2, pesquisas anteriores têm variado a pressão parcial da atmosférica para 0,3 MPa, como mostrado na Tabela 2.

A temperatura é um aspeto importante para a reação, no entanto, é necessário encontrar um número ideal, pois altas temperaturas desenvolvem difusão de CO_2, mas aceleram a evaporação da água e reduzem a solubilidade aquosa [31]. Além disso, o sequestro de CO_2 na pressão atmosférica é melhorado até a temperatura de ativação/cura de 60 ^oC. Acima dessa temperatura, a reação de CO_2 diminui [13]. A temperatura pode ser aplicada aquecendo o gás antes de o inflar ou colocando a câmara dentro de um forno. A duração da carbonatação varia de duas horas a vinte e oito dias em diferentes estudos e o desenvolvimento da propriedade aumenta com a duração da carbonatação [44]. A compactação da amostra ao moldar é importante, pois será homogénea e pode fornecer menos porosidade [56]. O processo de cura também muda entre estudos. Alguns investigadores testam as amostras logo após a carbonatação enquanto outros deixam curar até 35 dias [34]. A duração da carbonatação e a pressão de compactação são mostradas na Tabela 2. A configuração de carbonatação utilizada por Mahoutian et al. é mostrado na Figura 2.

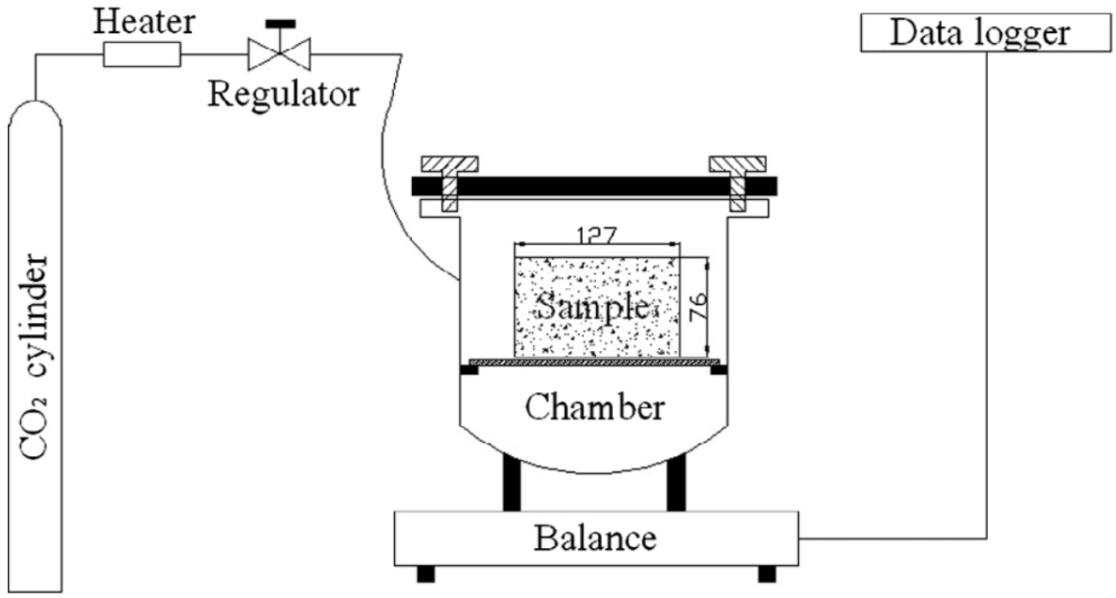

Figure 2 - Carbonation setup for carbon dioxide activated materials [34].

7.4. Materiais à Base de Escória de Aço Ativados por Carbonatação

Os materiais à base de escória de aço ativados por carbonatação são produzidos pela combinação de um pó de escória triturada e água sob as condições e procedimentos acima mencionados. Além de ser um material de construção sem cimento, podem armazenar dióxido de carbono e resíduos de escória de aço permanentemente. Entre os materiais ativados com dióxido de carbono, os estudos sobre o aglutinante vêm aumentando e há muitas informações disponíveis sobre suas propriedades mecânicas e microestruturas que confirmam a capacidade do ligante para aplicações estruturais. O aglutinante é usado como substituto tradicional de cimento Portland para outras aplicações que usam agregados naturais e resíduos para produzir materiais diferentes.

Mo e colaboradores, estudaram um betão ativado por dióxido de carbono que tinha como aglutinante 60% de escória de aço, 20% de cimento Portland e 20% de magnésia reativa e cal. Este betão não era cimentado nem apenas à base de escória, porém já mostrava o potencial aglutinante de escória de aciaria para aplicações concretas. Além disso, eles usaram escória de aço como agregados que mostraram melhor desenvolvimento de resistência à compressão em comparação com o betão que tinha agregados naturais. A maior resistência à compressão pode ser explicada devido à carbonatação da escória de aço que melhorou a interface entre os agregados e a matriz aglutinante [60]. Mahoutian e colaboradores desenvolveram outra aplicação, que era a produção de blocos de alvenaria ativados com dióxido de carbono à base de escória. Os blocos tinham apenas escória de aço como aglutinante e granito como agregado. Uma comparação com blocos tradicionais de alvenaria de cimento mostrou que os blocos de

alvenaria ativados com dióxido de carbono com escória de aço têm propriedades mecânicas e de durabilidade iguais e às vezes melhores. Além disso, as propriedades de lixiviação e o desempenho da resistência ao fogo satisfizeram um documento de referência das normas da Agência de Proteção Ambiental dos Estados Unidos e da ASTM, respetivamente. Além de reduzir as emissões de carbono e os resíduos depositados em aterros, a produção de blocos à base de escória foi economicamente viável [15]. A Mahoutian e Shao desenvolveram um bloco de construção de betão feito apenas com escória de aço como aglomerante e escória de alto-forno como agregados leves mostrando que blocos de construção carbono-negativos e sem cimento podem ser competitivos economicamente com o bloco de cimento tradicional se produzidos em escala industrial. Além disso, esses blocos não produzem resíduos, não consomem recursos naturais e possuem melhores propriedades mecânicas e de durabilidade [59].
Existem outras aplicações potenciais para materiais ativados com dióxido de carbono à base de escória que podem reduzir a zero os aterros de escória de aço e reduzir significativamente as emissões de dióxido de carbono em uma perspetiva global.

7.5. Estado dos Resultados Atuais da Pesquisa: Propriedades e Discussão

7.5.1. Resistência a Compressão

Ghouleh e colaboradores, num estudo, atingiram uma resistência à compressão de 80,5 MPa após 2h de carbonatação; enquanto Mahoutian e colaboradores, atingiram 39,5 MPa após 24h de carbonatação, evidenciando o comportamento não linear e o desenvolvimento de diferentes resistências à compressão, dependendo das propriedades do material, condições de carbonatação e procedimentos de projeto de mistura. Em alguns estudos, a resistência à compressão foi medida mesmo sem carbonatação da amostra, com o objetivo de descobrir se a mistura endureceria apenas pela hidratação [61]. Tais estudos alcançaram baixos resultados de resistência à compressão, representando a fraca reatividade de hidratação da escória de aço. Moon e Choi obtiveram resistência à compressão de até 29,1 MPa com apenas 5% de concentração de CO_2, mas misturaram 30% de cimento Portland com escória de aço e deixaram a cura por 28 dias a uma temperatura e humidade constantes [34]. Foram feitos dois painéis de escória de aço com EAF e uma mistura de escórias de aço EAF e BOF usando o mesmo processo e parâmetros. Ambos os componentes tinham composições químicas semelhantes, mudando apenas a sua finura onde a escória EAF era mais grosseira. O painel que continha uma mistura de escória de aço apresentou resistência à compressão 78% maior, mostrando que a finura da escória de aço é um parâmetro crítico em relação ao desenvolvimento da resistência à compressão do material [62]. Como mencionado anteriormente, comparar os resultados obtidos não é o mais apropriado, mas a interpretação completa de cada estudo ajuda a analisar que a resistência à compressão aumenta com maior pressão parcial do gás CO_2 [63], duração da carbonatação e com cura extra o ambiente de cura [48]. A maior resistência à compressão alcançada em cada estudo é mostrada na Tabela 3.

Table 3 - Compressive strength, CO_2, uptake, formed products and porosity of CO_2 activated materials.

Referência	Precursores	Resistência à compressão máxima (MPa)	Absorção de CO_2(%)	Produtos formados	Porosidade
[22]	BOFS	110.6	0 - 13.22	C-S-H $CaCO_3$	
[37]	Escória de Aço	9		$CaCO_3$	
[34]	Escória da concha	39.5	4.0 - 12.8	C-S-H C-A-H $CaCO_3$	
[25]	Escória EAF	20.1	1.7 - 4.6	C-S-H $CaCO_3$ Ca(OH)	
	Mistura de escórias EAF e BOF	35.9	3.3 - 4.8	C-S-H $CaCO_3$ Ca(OH)	
[38]	Escória de Aço	44.1	0 - 17.6	$CaCO_3$	15.7 - 33.6
[39]	Escória de Aço	29.1	13 - 17	$CaCO_3$	34 - 38.3

[a] O intervalo de valores é compilado devido ao mesmo uso de estudo de várias misturas ou condições de carbonatação

Além do caso de 9 MPa, os resultados mostram que os materiais ativados com dióxido de carbono à base de escória de aço têm um bom potencial como um substituto de cimento Portland para aplicações pré-moldadas.

7.5.2. Absorção de Dióxido de Carbono

A análise de absorção de dióxido de carbono, como era esperado pelos autores, seguiu o comportamento da resistência à compressão. Amostras com alto desenvolvimento de resistência à compressão apresentaram maior captação de CO_2 [44]. A absorção de CO_2 também aumentou devido à duração da carbonatação. Duas misturas diferentes deixadas por 2 e 24 horas de carbonatação mostraram um aumento entre 30-50% na absorção de CO_2 [25]. Siriwardena e Peethamparan descobriram para o GGBFS uma absorção de CO_2 bastante baixa, variando de 1,32-1,83%. Descobriram, também, que, adicionando água, a quantidade de CO_2 aumenta. Entretanto, nenhum teste de resistência à compressão foi realizado e a escória utilizada foi como recebida, não mencionando a finura, que pode ser uma razão para essa baixa captação [32]. Alguns autores não mediram este parâmetro, no entanto, a maior absorção de CO_2 alcançada foi de 17,6% em massa [61], o que representa um valor interessante para reduzir significativamente a quantidade de CO_2 na atmosfera e minimizar os efeitos do aquecimento global. A Tabela 3 também mostra a absorção de CO_2 dos estudos em revisão.

7.5.3. Microestrutura

A análise microestrutural ajuda a caracterizar os poros e distinguir quais foram os produtos formados e consumidos, além de analisar o aglomerante e sua composição em boa escala.

7.5.3.1. Caracterização de Poros

Apenas Mo e colaboradores caracterizaram os poros e descobriram que, com a carbonatação e consequentemente a produção de calcita ($CaCO_3$): o volume total de poros, o tamanho máximo e médio dos poros diminuiu significativamente, o que aumenta a resistência à compressão. Comparando um ligante de escória de aço antes e depois da carbonatação, a amostra não carbonatada tem três vezes mais diâmetros de poros grossos e quase 50% mais de volume total de poros do que uma amostra carbonatada de um dia. Além disso, comparando a amostra não carbonatada com uma amostra carbonatada de catorze dias, o diâmetro do poro grosso pode ser reduzido até trinta vezes e o volume total do poro em 2,5 vezes. [26]. A Tabela 3 mostra também a faixa de porosidade alcançada.

7.5.3.2. Produtos Formados

Como era esperado, todos os estudos descobriram a produção do carbonato de cálcio $CaCO_3$ que forneceu aos ligantes propriedades de ligação, resistência à compressão e redução de porosidade. Além disso, alguns outros produtos também foram formados, como hidrato de silicato de cálcio e hidrato de cálcio-aluminato devido à hidratação [22]; materiais do grupo cancrinito carbonato-oxalato formados devido ao aumento da duração da carbonatação [25]; Calcita e nesqueonite magnesiana que resultaram da carbonatação da combinação de MgO e CaO [64]. Mahoutian comparou as curvas termogravimétricas e termogravimétricas diferenciais para três diferentes condições de cura, 35 dias de hidratação, 24h de carbonatação e 35 dias de hidratação após 24h de carbonatação. A Figura 3, evidenciou que três produtos diferentes foram formados em quantidades diferentes, dependendo das condições de carbonatação pelos picos DTG.

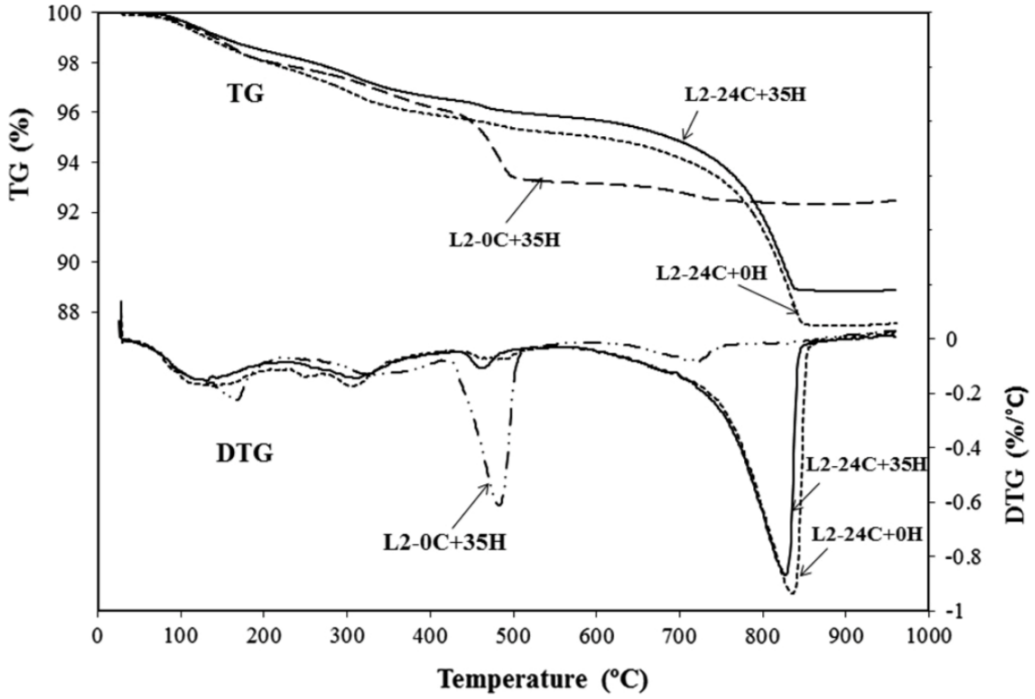

Figure 3 - Thermogravimetric and differential thermogravimetric curves of the steel slag binder (L2) after different curing conditions: 35 days of hydration (H), 24 hours of carbonation (C) and 35 days of hydration after 24 hours of carbonation (Mahoutian et al., 2014).

A faixa de temperatura de 105-400 ºC representa a perda de água da primeira desidratação de hidratos de silicato de cálcio (CSH) e hidratos de aluminato de cálcio (CAH), que é bastante semelhante em todas as diferentes condições. A perda de massa entre 400-500 ºC representa uma perda de água devido à desidratação do Ca (OH) (CH), produto da reação entre a escória de aço e a água que não é percebida na única condição de carbonatação. O intervalo de 500 a 900 ºC representa a perda de CO_2 devido à descarbonatação de carbonatos de cálcio. A única mistura hidratada não apresentou formação de carbonato de cálcio, quantidade elevada de CH, mas não formação suficiente de CSH para o desenvolvimento de ligações fortes na pasta, o que evidencia o baixo comportamento hidráulico da escória de aço. Por outro lado, a alta reatividade do dióxido de carbono foi evidente devido à formação de carbonato de cálcio em ambas as amostras carbonatadas. Mo e colaboradores realizaram análise por microscopia eletrónica de varredura e confirmaram, em escala microscópica, uma amostra carbonatada com calcita e hidrato de silicato de cálcio como produtos no aglomerante resultante, como mostrado na Figura 4. Na Tabela 3, os produtos formados são mencionados [63].

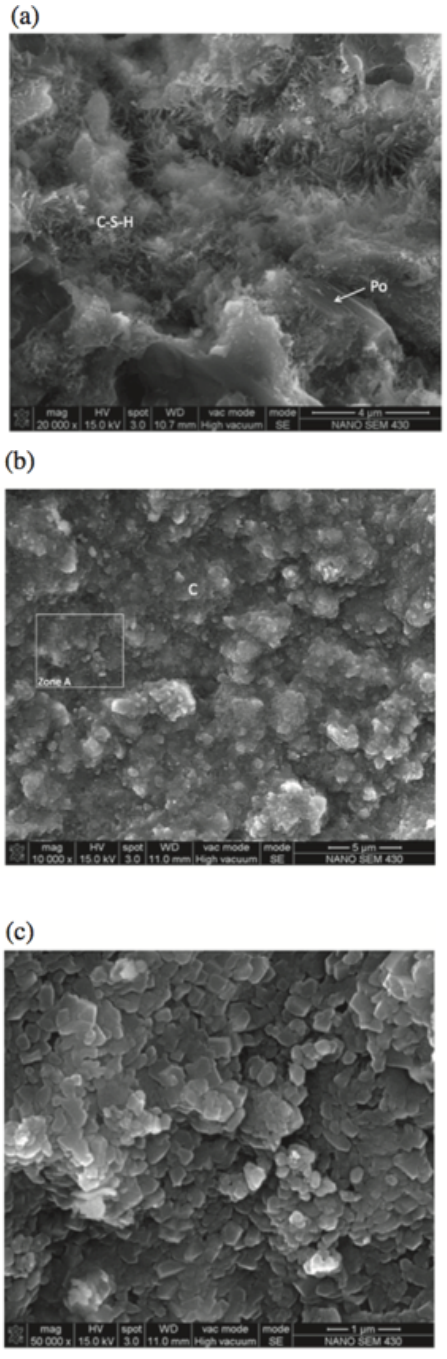

Figure 4 - SEM image of steel slag pastes before and after CO_2 curing: (a) steel slag paste, before CO_2 curing; (b) steel slag paste, after 14 d of CO2 curing; and (c) calcium carbonate formed in steel slag paste, closer look at Zone A in (b) [63].

7.5.3.3. Fases Mineralógicas

As fases mineralógicas que são analisadas através da difração de raios X também confirmam a formação de alguns produtos. Além disso, mostra as fases consumidas, que são principalmente C_2S, no entanto, alguns C_3S e mayenite ($C_{12}A_7$) também foram consumidos [34]. Ghouleh e colaboradores, também descobriram que, quando a amostra é hidratada antes da carbonatação, é possível ver a portlandita e também alguma periclase (MgO) sendo consumida [22]. Por outro lado, a análise de difração de raios-X mostrou algumas fases que não reagiram sob carbonatação como gehlenite e merwinita e, além delas, a brownmillerita mostrou baixa reatividade [34]. A Figura 5 mostra análises de difração de raios-X comparando as diferenças de fase mineralógica entre a escória de aço bruta, uma única escória de aço hidratada e a amostra carbonatada e hidratada, distinguindo a análise do núcleo e da borda individualmente. x γ-C_2S foi principalmente observado na escória bruta que é um silicato de cálcio não hidráulico, no entanto, alguns ß-C_2S, nomeadamente um silicato de cálcio hidráulico, também foram encontrados. Quando comparado com a única amostra hidratada, vê-se que apenas ß-C_2S foi consumido produzindo Ca (OH) que não possui propriedades de ligação. Por outro lado, as amostras carbonatadas apresentaram o consumo de γ-C_2S além do ß-C_2S, que originou a produção de carbonato de cálcio. Como esperado, o núcleo foi menos ativado que a borda, uma vez que a borda tem contato direto com a atmosfera rica em CO_2. Alguns γ-C_2S não reagidos também foram encontrados na análise de XRD.

7.6. Desenvolvimentos Recentes Relacionados à Indústria

A ciência e a indústria têm trabalhado com o mesmo objetivo: reduzir a pegada de carbono, reduzindo as emissões de CO_2 no processo betão. Além de produzir alguns materiais ecológicos, esses ligantes e betões também têm boas propriedades mecânicas.

Duas patentes dos Estados Unidos da América referem-se a materiais que após a carbonatação mostram boas propriedades. Num deles, os materiais cimentícios ricos em cálcio são carbonatados, misturados com água e depois usados como adição para produzir betões que têm menos emissões de CO_2 em seu processo. Um dos objetivos é reduzir as emissões de CO_2 na indústria de betão usando esta suspensão carbonatada como uma adição que é feita antes do cimento Portland comum, agregados e outros materiais serem misturados [65]. O material também é usado como elemento de ligação ou matriz no núcleo, primeira ou segunda camada da estrutura do material. Mesmo o sistema considerado deveria ser otimizado, já possui boas propriedades mecânicas, térmicas, magnéticas, óticas e nucleares. O método de fabrico também é definido e descrito por [66]. Como esperado nos materiais carbonatados, o principal produto da reação é a calcita ($CaCO_3$), que proporciona melhorias na propriedade mecânica da estrutura final.

A indústria seguiu a ciência tentando reduzir a pegada de carbono através da fabricação de betão. Algumas empresas desenvolveram ideias e processos que produzem aglomerantes sem cimento ou até materiais complementares de cimento para substituir parte do cimento nas tradicionais misturas de betão. A Novacem é uma das empresas que é usada para produzir um aglutinante sem cimento feito por um material de óxido de magnésio que captura CO_2 quando misturado com água em um ambiente de CO_2. O principal produto do aglutinante Novacem foi o carbonato de magnésio, responsável pela sua resistência [67]. A Solidia é outra empresa que possui um cimento não hidráulico que é ativado pela reação de CO_2 e silicatos de cálcio sob condições específicas. Como esperado, a calcita e a sílica são os principais produtos e responsáveis pela resistência e resistência ao craqueamento do material. O cimento Solidia pode reduzir a pegada de carbono do processo de betão em 70% e tem condições de fundição como os betões comuns de cimento Portland padrão [68]. A Calera é outra empresa que produz um sistema de aglutinante ativado por carbonato de cálcio CO_2 para produtos de betão. Este cimento é livre de qualquer cimento Portland comum e tem maior resistência à compressão. Além do sistema aglutinante, a empresa também produz o carbonato de cálcio como um material cimentício suplementar que substitui cerca de 15% do cimento Portland na mistura de betão [69]. O Carbon Cure é outra empresa nesta área que tem uma aplicação ligeiramente diferente, CO_2 capturado de processos industriais são inflados em cimento Portland com água. A carbonatação é responsável por aumentar entre dez a vinte por cento da resistência dos materiais, no entanto, a quantidade final de redução de emissão de CO_2 é de cerca de cinco por cento em comparação com uma produção de cimento comum de betão comum [70].

Essas empresas demonstraram quão eficientes e possíveis os ligantes e betões ativados por carbono são baseados nas propriedades e uso de CO_2. No entanto, esse processo é limitado apenas para aplicativos pré-fabricados. O uso de muitos resíduos ricos em cálcio e magnésio é o principal desafio para futuras pesquisas. Os custos devem ser cuidadosamente analisados com base em unidades de produção em escala industrial, pois são necessários padrões para tornar o material confiável para a sociedade.

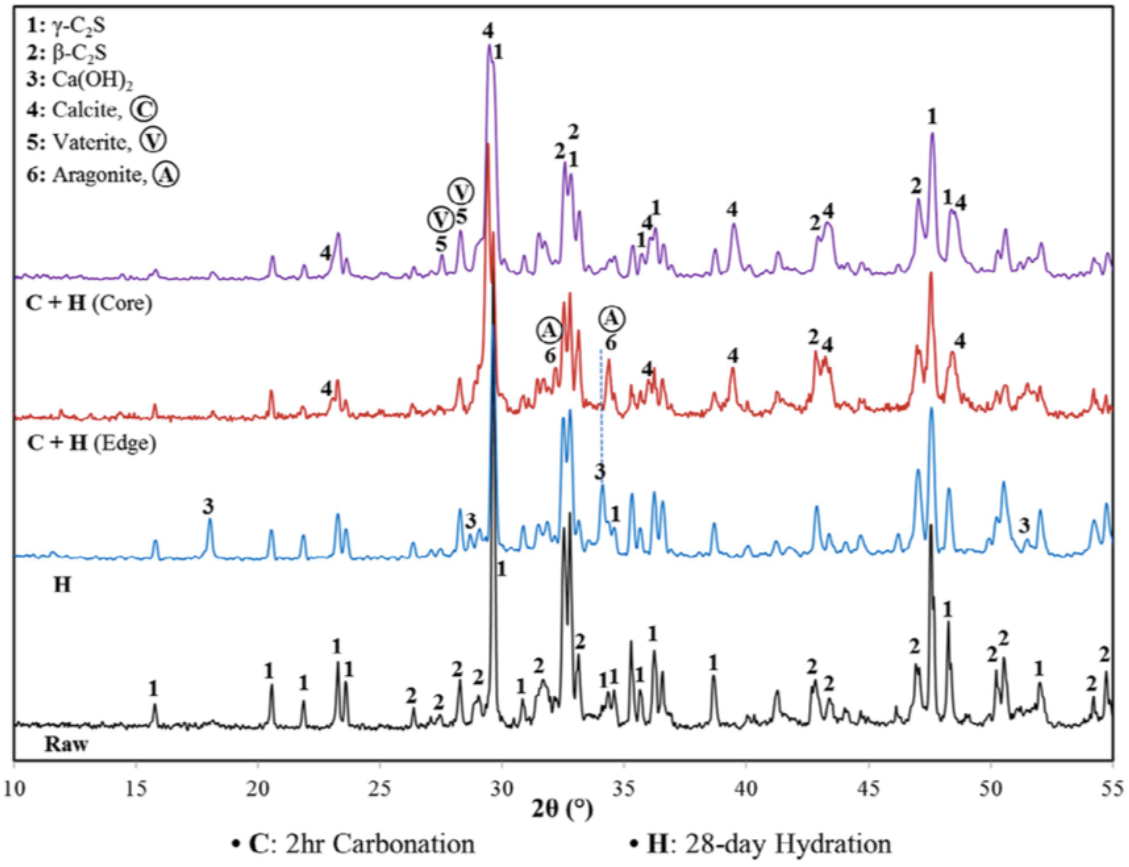

Figure 5 - XRD spectra from a steel slag comparing different curing scenarios with the raw material [22].

Abstract

The scope of this thesis is the synthesis and characterization of binders produced with steel slag from the National Steel Industry, in Maia and Seixal, Portugal, and activated by accelerated carbonation curing. This doctorate thesis presents an extensive study over this technology beginning with the state-of-the-art discussion, evidencing the most relevant studies about the topic, as well as systematically identifying the research aspects which must be further investigated and consequently approached on this thesis.

The steel slag from the National Steel Industry has its properties characterized by a different analysis which determined its density and fineness. An elemental characterization was possible through a scanning electron microscopy analysis, an X-ray diffraction analysis was done in order to characterize the steel slag mineralogical phases.

The sample preparation process is discussed in detail highlighting the phases of drying, milling, grain size separation, mixing, and compaction. Performing these steps ensures compliance and reliability of results, plus influences the final product properties allowing optimal conditions parameterization and final product improvements by manipulating each process phase parameters. A study related to the use of additives on the steel slag hardening process with carbon dioxide (CO_2) curing is also evidenced and compared with relevant research in correlated areas.

A wide study about the accelerated carbonation curing conditions was performed which evidenced the controlled parameters and the respective influence on the final results by manipulating each of them. Oven temperature, system total pressure, curing duration, and humidity were the investigated parameters and had their respective effects systematized. In addition, with the CO_2 curing, an analysis of the effect of complementary curing methods on the binder's compressive strength development was carried on. The carbonated steel slag binders were subjected to complementary curing for the specific duration under four different conditions: in an oven, moisture room, plastic bag and under water. The complementary curing effects were exposed and discussed.

The microstructure characterization of steel slag-based binder activated by CO_2 was performed by scanning electron microscopy analysis, X-ray diffraction analysis and thermogravimetric analysis, accomplishing the identification of the formed products on the steel slag carbonation.

The study defined optimal activation conditions and applied the same conditions to the Portland cement for comparison purposes. Moreover, Portland cement had its characterization performed.

Keywords

Steel Slag, Carbon Oxide Activation, Sustainable Building Materials, Clinker-Free Building Materials.

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Chapter 1
Introduction

1. Overview

The following study was conducted aiming to tackle an economic and environmental concern that is occurring not only in Portugal but worldwide in every steel manufacturer. The steel slag is a by-product which is produced in large scale and has limited use such as aggregates for roads and railway infrastructures. However, on one hand, its utilization as aggregates does not exploit the potential economic value that the steel slag can have been given for free or sold for a symbolic price. On the other hand, its utilisation does not require as much steel slag as it is produced and it is mainly dumped at landfills which is costly, immobilize a productive area and may provoke an environmental accident. Figure 1 evidence a steel slag landfill.

Figure 1 - Landfill

The potential of using steel slag as a binder replacer for precast building applications was investigated by doing the following steps: grinding the received steel slag; sieving and separating the grinded slag; mixing the sieved powder with water; moulding by compacting the blend; and curing the fresh samples under specific conditions to get hardened through carbonation. The main academic value of this research is to guide the academia on the carbon dioxide activation of steel slag providing information regarding properties, conditions and

additives such as slag fineness, water to solid ratio, compacting pressure, system total pressure, oven temperature, carbonation duration, ethanol utilisation, sodium chloride utilisation, sodium bicarbonate utilisation, grinded glass utilisation, plastic bag curing before carbonation, plastic bag curing after carbonation, plastic bag curing before and after carbonation, moisture room curing before and after carbonation, underwater curing after carbonation, oven curing after carbonation.

2. Research Objectives

Therefore, this doctoral thesis has the following general objectives:

- Study a novel CO_2-activated steel slag-based binder by combining steel manufacturing by-products with other mineral and non-mineral wastes;
- Analyse and characterize CO_2-activated binders with potential for precast buildings applications;
- Write the final document based on developments and studies conducted.

The CO_2-activated binder consists of steel slag and other wastes that are enriched with calcium and silica activated in an atmosphere with captured CO_2. It is possible to reduce the Portland cement consumption, thus also reducing the CO_2 emissions and the embodied energy and permanently storing CO_2 through the carbonation that will activate the binder. Soon may be possible to have this and others environmental friendly precast building materials included on building designs.

Thus, the specific objectives of this work are:

1) Analyse Portuguese steel slag chemical compositions and verify its carbonation conditions. For this purpose, an experimental process of binder preparation will be established, processing by moulding and pressing, curing under pressure in a CO_2 chamber:
    - To study the chemical composition of Portuguese steel slag;
    - To study the exposure conditions as System total pressure, temperature and CO_2 source;
    - To study the properties of the wastes as particle size and surface area.
    - To study the CO_2-curing conditions as System total pressure, chamber temperature and curing durations;
    - To study the CO_2 uptake capacity and efficiency;
    - To determine the chemical composition by energy dispersive spectrometry (SEM/EDS) and X-ray diffraction (XRD) analyses.
2) Analyse other wastes chemical compositions that would improve the carbonation conditions as an additive:
    - To study the compatibility of these wastes with the main used wastes for improving the carbonation conditions;

- To determine potential additions that will be in the binder blends.

3) Define different blends and procedures and test its carbonation with specific activation and cure conditions:
   - To determine carbonation procedures to be followed with the binder blends;
   - To determine the chamber conditions to be applied with the binder blends;
   - To determine the blends composition and the mass ratio of each content;
   - To test all mixtures with all different defined procedures;
4) Analyse mechanical properties of the defined binders:
   - To analyse the binder's microstructure;
   - To analyse the thermogravimetric analysis (TGA) results;
   - To determine the binder's compressive strength;
   - To determine the chemical composition by (SEM/EDS) and (XRD) analyses.
5) Write the final document based on developments and studies conducted.

3. Thesis Structure

This doctoral thesis has been divided into six different chapters which present and discuss:

- Chapter 1 – the introduction, evidencing the study, its justification and relevance;
- Chapter 2 – the state of the art, evidencing the previous study that has been done before this research;
- Chapter 3 – experimental procedure, evidencing in detail the work that has been conducted;
- Chapter 4 – materials and methods, characterizing the materials and highlighting the conditions;
- Chapter 5 – results and discussion, analysing and interpreting the outcome from the research;
- Chapter 6 – conclusion, evidencing the relevant findings and suggesting complementary research to be conducted regarding steel slag-based binders activated by carbonation.

Chapter 2
CO_2 - Activated Steel Slag-based Materials: A Review

1. Preface

This chapter discusses the state-of-art of carbon dioxide (CO_2) activated steel slag-based materials evidencing previous research that has been conducted in the area, highlighting main outcomes, findings, and opportunities for further research.

2. Introduction

2.1. Global Warming and CO_2 Production

Global Warming is caused by the production and accumulation of Green House Gases (GHGs); therefore, finding efficient methods for reducing its production, implementing its capture and storage systems is compulsory. GHGs include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluorocarbon (F_6C). Nowadays, the most abundantly emitted GHGs are CO_2 (56%) and CH_4 (18%) [1].
Global Warming exceeded its limits in 2015, mainly due to a high content of carbon dioxide (CO_2) in the atmosphere [2]. CO_2 emissions of 4,45 billion tons of CO_2-equivalents in 2015 [3] from a spectrum of industrial processes pose negative impacts on the environment and human health.
Regarding CO_2 production, fossil fuel power plants are the largest sources (40% of total CO_2 emissions). Other sources of CO_2 arise from transportation and general industry [3]. Regarding the construction sector, the Portland cement industry is responsible for emitting 15% of the indirect CO_2 emissions from non-energy use. Moreover, its production process consumes a huge amount of energy [4].

2.2. Steel Slag Production

European economic activity and households produced 2.5 billion tons of waste in 2014. Most of this waste was dumped in landfills resulting in potential long-term public health problems, and soil and water contamination [5]. This waste management behaviour results in the accumulation of a large amount of mineral waste deposited in fields which leads to environmental pollution and serious landscape impacts which affect the quality of life of the local population. Preventive measures typically involve the use of earth/rock dams or lagoons to store waste. Unfortunately, the potential collapse of such structures could have serious impacts on the environment and human health and safety [6]. The steel industry has an accumulation problem

regarding the waste produced at its steelmaking process, the steel slag is the main by-product which is produced at a large scale. The steelmaking process uses three different furnaces. The basic-oxygen furnace (BOF) is used at the first steel refinement of the steelmaking process with molten iron, steel scraps plus lime or dolomite as input. The electric-arc furnace (EAF) has a similar steel refining process but uses high-power electric arcs to produce high-quality steel from recycled steel scrap. After being refined by the BOF or EAF, the steel can be refined again through a secondary steel making operation which aims to achieve a specific chemical composition. This secondary operation uses the ladle furnace which is similar to the EAF and has ladle slag as a by-product [7]. The steel slag annual production worldwide is about 130 million tons which are mainly Electrical Arc Furnace (EAF) and Basic Oxygen Furnace (BOF) slags [8]. Most part of this production is disposed of in landfills. However, part of the slag production is destinated to be used as aggregates for different construction purposes such as ready-mix concrete, asphaltic concrete, road bases, and surfaces, and fills [9].

2.3. Steel Slag-Based Materials Obtained by CO_2 Curing / Activation

There are numerous studies about the carbonation of Portland cement-based materials such as the review where Ashraf summarized relevant information of these carbonation features and highlighted areas where further investigation could be taken [12]. Besides this general approach, Jang et al. focused the research on CO_2 sequestration [13] and Zhang et al. analysed the application of carbonation through its curing mechanism, achieved properties and feasibility [14].

Steel slag used as an alternative recycled raw material activated by CO_2 is being recently studied and considered as a solution for storing CO_2, reducing GHG emissions, as well as recycling and valorising steel industry waste. A challenge on the steel slag-based carbon dioxide cured/activated materials is related to the variety of its chemical composition which depends on the steel manufacturing specification. Different benches of slag have a different chemical composition and structure, thus making the carbonation reaction more difficult to model and understand [15].

2.4. Gaps in Knowledge and Objectives

Recently, studies have shown that the steel slag will react with aqueous CO_2 under controlled conditions to form complex carbonates which have binding capabilities. The compressive and flexural strength of the analysed cement-free binder systems increases with the carbonation duration. Moreover, the systems exhibit mechanical properties that are comparable to ordinary Portland cement systems, which are commonly used as the binder in the construction industry [38].

Therefore, apart from the cement-based, this review aims to emphasize the current research status on steel slag-based construction materials activated by carbonation. This review also covers the reaction, carbonation conditions, carbon dioxide uptake, carbonation products, compressive strength, materials properties, different construction material applications, and research needs. Information was obtained from well-known journals and researchers who have recently been working with slag-based carbon dioxide activated materials.

3. Steel Slag Composition and Carbonation Reactivity

Steel slag is the main by-product from the steel manufacturing and often dumped into landfills. In Europe, road construction activity uses an expressive amount of slag as aggregates. In 2012, almost half of the produced slag was used. However, there is still a large amount of slag which has not been reused nor submitted to a recycling process [16].

The chemical composition of steel slag depends on the steelmaking process which is also an important factor for its CO_2 reactivity. Basic-oxygen furnace (BOF) slag has calcium, iron and silica oxides as the main components. The iron oxide (FeO/Fe_2O_3) can be up to 38%, silica (SiO_2) range from 7 to 15% and the calcium oxide (CaO) is the highest compound ranging from 36 to 60% [17].

Electric-arc furnace slag has a similar composition to basic-oxygen furnace slag because of its similarities on the production processes. However, as it uses recycled steel scraps, the electric-arc furnace slag chemical composition also depends on steel scrap properties. The iron content can be up to 40%, SiO_2 is about 16% and the CaO is not the highest compound as in the basic-oxygen furnace slag ranging from 23 to 38% [18,19].

As the ladle furnace process is secondary and with some alloys, this slag differs more from the basic-oxygen furnace than the electric-arc furnace, depending on the type of steel produced. The FeO content is much lower, being less than 5%, SiO_2 can be almost 20% and the CaO is also higher ranging from 42 to 57% [20]. Table 1 shows the chemical composition of steel slags from different studies which confirm the wide variability of its composition.

Table 1 - Steel slag: types and oxide compositions (%)

Reference	Type	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3
[21]	BOFS	47.9	12.2	1.2	0.8	—
[22]		61.21	24.92	1.83	4.89	3.04
[23]		36.4-45.8	10.7-15.2	1-3.4	4.1-7.8	—
[24]		47.5	11.8	2.0	6.3	22.6
[25]		39.08	12.47	6.87	10.57	19.48
[26]		42.42	11.04	1.61	7.19	27.37
[27]		39.3	7.8	0.98	8.56	38.06
[18]		45.0	11.1	1.9	9.6	10.9
[17]		47.7	13.3	3.0	6.4	24.4
[28]		23.9	20.75	0.84	3.775	—
[19]	EAFS	24.4	15.4	12.2	2.9	—
[25]		35.23	9.41	10.78	9.77	24.22
[29]		23.9	15.3	7.4	5.1	—
[18]		38.8	14.1	6.7	3.9	20.3
[30]		35.7	17.5	6.3	6.5	26.4
[31]	GGBS	65.04	20.71	4.83	1.03	2.77
[32]		39.80	36.00	10.53	7.93	0.67
[33]		42.5	31.9	13	4.81	0.34
[34]	LFS	65.23	12.35	16.55	3.96	0.79
		57.55	6.21	23.17	5.04	3.55
[35]		49.6	14.7	25.6	7.9	0.22
[36]		49.5	19.59	12.3	7.4	0.9
[20]		50.5-57.5	12.6-19.8	4.3-18.6	7.5-11.9	1.6-3.3
[18]		42.5	14.2	22.9	12.6	1.1
[37]	Steel Slag	51.05	25.80	2.31	9.32	0.72
[38]		42.42	11.04	1.61	7.19	27.37
[39]		54.30	17.70	6.40	9.20	3.00
[40]		45-60	10-15	1-5	3-13	3-9
[25]	Mix of EAF and BOF slags	39.08	12.47	6.87	10.57	19.48

[a] The range of values is compiled based on the chemical composition data from different sources

— = data not available.

The steel slag does not have a good hydraulic property. Due to its SiO_2 content, it is amorphous and the little number of tri-calcium silicates are presented in its mineralogical phases [41]. Therefore, the steel slag binding potential and contribution on compressive strength in Portland cement systems is not significant for conventional hydration/moist methods. Another drawback of the steel slag replacement and use on traditional cement is its inordinate expansion and

volume instability over time caused by the high content of free-CaO/MgO [42]. However, this expansion can be avoided or reduced by carbonating the steel slag due to the consumption of free-lime content, the main expansible phase [43].
Steel slag has high carbonation reactivity due to its free-CaO/MgO content, making the slag a good raw-material for construction materials activated by carbonation [44]. Together with the free-CaO/MgO, hydraulic calcium silicate (Ca_3SiO_5 (C_3S), ß-Ca_2SiO_4 (C_2S)), non-hydraulic calcium silicate (γ-C_2S, $CaSiO_3$ (CS)), and Portlandite (hydration products of free-CaO or calcium silicate) are also reactive components for steel slag carbonation [22]. These reactive components provide the formation of the calcium/magnesium carbonates and calcium silicate hydrates which are the main phases responsible for the binding capacity and compressive strength development [45]. Therefore, LF slag due its chemical composition rich in calcium oxide suggest the most suitable for carbonation.

4. Carbon Dioxide Material Activation

Carbonation is a chemical reaction between different silicates and CO_2 that produces mainly carbonates with binding properties. Carbonation also contributes to enhancing the mechanical properties and durability of the materials while storing and using CO_2 as a source of the reaction [13]. In general, materials can be carbonated with different purposes such as CO_2 storage, concrete property improvement, and carbon dioxide activated binder development [12]. For carbon dioxide activated materials, carbonation also has the hardening role.

4.1. Mainly Reactive Compounds

The carbonation process of steel slag includes three main reactions: hydration and dissolution of CO_2, leaching of Ca^{2+} and Mg^{2+}, and precipitation of carbonates. CO_2 firstly diffuses into the paste and dissolves in pore solution to form carbonic acid (H_2CO_3).
Then, the reaction is followed by ionization of H_2CO_3 to HCO_3^-, CO_3^{2-} and H^+ ions as can be seen in Eq. (1) [33].

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \quad (1)$$

Subsequently, the reaction of CO_3^{2-} with Ca^{2+} and Mg^{2+} ions leaching out from the steel slag results in the formation and precipitation of calcium and magnesium bearing carbonates as shown in Eq. (2) and (3) [46].

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (2)$$
$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \quad (3)$$

At the presence of Mg^{2+}, magnesian calcite with the incorporation of Mg^{2+} into the $CaCO_3$ may be formed in carbonated pastes, but it is hard to be distinguished with XRD due to overlapped patterns of magnesian calcite and calcite. [26].
The slag mixed with water in a carbon dioxide environment represents the carbonation which occurs for the carbon dioxide activated/cured materials where different calcium silicates such as Alite (C_3S), Belite ($\gamma/ß$-C_2S) are carbonated and hydrated at the same time. Such can be described through Eq. (4) and (5), where calcium carbonates and calcium silicate hydrates are formed as the main reaction products of steel slag carbonation [47].

$$2(3CaO \times SiO_2) + 3CO_2 + 3H_2O \rightarrow 3CaO \times 2SiO_2 \times 3H_2O + 3CaCO_3 \quad (4)$$
$$2(2CaO \times SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO \times 2SiO_2 \times 3H_2O + CaCO_3 \quad (5)$$

After moisturizing, some products can be carbonated too. Such happens with the calcium hydroxide and the calcium silicate hydrates. The carbonation of calcium hydroxide occurs based on three reactions; the main reaction is expressed as in Eq. (6) [13].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (6)$$

The calcium silicate hydrates (CSH) carbonation initiates after the consumption of the calcium hydroxide during the reaction. This reaction is not completely defined and can be expressed as follows in Eq. (7) [48].

$$xCaO \cdot ySiO_2 \cdot zH_2O + xCO_2 \rightarrow xCaCO_3 + y(SiO_2) \cdot H_2O) + (z - yt)\, H_2O \quad (7)$$

Related researches with different CO_2-reactive wastes found that the carbonation can happen also with iron (Fe) in an aqueous environment and can be seen in Eq. (8) [21].

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \quad (8)$$

4.2. Carbon Dioxide Uptake by Steel Slag Activation

The CO_2 uptake capacity of a material can be calculated with a theoretical formula [49]. Then, it is possible to predict the carbonation depth and calculate the volume of the carbonated concrete. Finally, this volume should be converted into the amount of CO_2 uptake [50]. Studies have estimated up to 52% of CO_2 uptake by carbonating different calcium-rich wastes [51]. The theoretical uptake capacity can also be predicted based on the chemical composition of the material, through the Steinour's formula in Eq. (9) [13] or Huntzinger's formula in Eq. (10) [52].

$$CO_2 \text{ uptake } (\%) = 0.785(CaO - 0.7SO_3) + 1.09Na_2O + 0.93K_2O \quad (9)$$

$$CO_2 \text{ uptake } (\%) = 0.785(CaO - 0.56Ca(CO_3) - 0.7SO_3) + 1.091MgO + 0.71Na_2O + 0.468K_2O \quad (10)$$

Once Steinour's formula does not consider the magnesium content which also can be carbonated, the Huntzinger's formula suggest to be more adequate to calculate the CO_2 uptake capacity. As slags have a nonlinear mineralogical phase and chemical composition, their maximum uptake capacity might not be calculated or easily predicted. The real uptake capacity will depend on the slag powder fineness and the carbonation conditions. Moreover, the steel slag can achieve up to 75% of its theoretical maximum uptake based on its mass [53].
Experimental methods can find real CO_2 uptake through different analysis and calculations. The mass gain and mass curve are common ones. On the mass gain method, it is possible to quantify the amount of CO_2 absorbed by the material, comparing the difference between the mass before and after the carbonation. At the curve method, there is an advantage when measuring the CO_2 uptake from the beginning to the end of the carbonation process and using it as a tool to evaluate the consistency of the results of the mass gain method. The mass gain and the mass curve method equations are respectively (11) and (12): [54].

$$CO_2 \text{ uptake } (\%) = (\text{Final mass} + \text{Mass of water loss} - \text{Initial mass})/\text{Mass of dry slag} \quad (11)$$

$$CO_2 \text{ uptake } (\%) = (\text{Residual mass} - \text{Second residual mass})/\text{Mass of slag} \quad (12)$$

Another experimental method is the CO_2 analyser which measures the CO_2 uptake by comparing the difference in the carbon content (CC) between a carbonated and non-carbonated sample as seen through the following equation (13): [22]

$$CO_2 \text{ uptake } (\%) = (\text{CC in carbonated slag} - \text{CC in non-carbonated slag})/\text{Mass of dry slag} \quad (13)$$

Another uptake method is related to pressure drop in the carbonation chamber with the chamber volume and the temperature which is demonstrated in Eq. (14). However, as the pressure varies with temperature, this method should be carefully calculated: [33]

$$nCO_2 = (\text{Pressure drop} \times \text{Chamber volume})/\text{Universal gas constant} \times \text{Temperature} \quad (14)$$

The universal gas constant is 8.31×10^{-3} L x bar/K x mol.
Researchers also use indirect methods to analyse the efficiency of carbonation on their samples such as thermogravimetric analysis (TGA) and X-ray diffraction (XRD). It shows the originated products from the carbonation reaction by the analysis of the mass loss curves and the mineralogical phase diagrams [32].

4.3. CO_2 Uptake Conditions and Procedures for Steel Slag Activation

The CO_2 uptake conditions are important to be controlled and understood because it affects the kinetics of the carbonation reaction and has a strong influence on the development of the properties of the material. The water content of the mixture is a critical parameter because it influences the reactivity. Moreover, the carbon dioxide diffusivity through the sample depends on the free water present in the matrix pores [55]. The optimal water to the solid ratio for achieving higher carbonation degree depends on the fineness of the slag [31]. The water to slag ratio used in different research studies is shown in Table 2. By controlling the relative humidity, a more efficient activation is reached. In general carbonation, the optimal condition was found when the relative humidity was between 50-70% for an effective reaction [13]. Besides improving the CO_2 diffusion, the humidity causes further hydration of non-reactive phases [56]. However, researchers who have been developing carbon dioxide activated materials have not controlled this parameter during their experiments.

The slag fineness has a strong influence on the carbon dioxide activation when the particle size is smaller, the surface area is bigger favouring slag reactivity and carbonation conditions [43]. Slag Blaine fineness of previous studies is also shown in Table 2.

The carbon dioxide activation efficiency has a high dependence on the CO_2 concentration, its dependence can be confirmed by the compressive strength development for different concentrations. Researchers have found that for 20.0% of CO_2 concentration, which simulates the industrial tail gas, is responsible for the compressive strength development being more than three times lower compared with a gas of 99.9% of CO_2 concentration, both with six hours of carbonation duration [58]. Therefore, a source of highly concentrated CO_2 increases the carbonation rate by ambient CO_2 concentration. Besides the concentration, the System total pressure has influence into its diffusivity, since the material matrix is carbonated at low pressure, precipitation of calcium carbonate decreases the porosity, inhibiting the CO_2 diffusivity. Meanwhile, some CO_2 is diffused in the matrix at high pressure before the pores are closed by calcium carbonate [60]. For CO_2 activated binders, previous researches have been ranging the total pressure from atmospheric to 0.3 MPa as shown in Table 2.

Table 2 - Carbonation conditions of recent researches on carbon dioxide activation.

Reference	Material	Water to Solid ratio	Blaine Number (m^2/kg)	CO_2 Concen-tration (%)	Pressure (MPa)	Carbonation Duration (h)	Compacting Pressure (MPa)
[22]	Binder	0.15	316		0.15	2-24	16
[37]	Binder	0.125		100	0.3	1	0.5
[34]	Binder	0.1	247 - 318		0.15	24	12.5
[15]	Masonry block	0.18 - 0.2	239		0.15	24	12
[25]	Slag panel	0.08	178		0.15	2 - 24	12.5
	Slag panel	0.08	178-239		0.15	2 - 24	12.5
[38]	Binder	0.4		99.9	0.15	24 - 336	
[39]	Binder	0.5	359	5		168 - 672	

The temperature is an important aspect of the reaction. However, it is necessary to find an optimal number as high temperatures develop CO_2 diffusion but speed the water evaporation and reduce the aqueous solubility [59]. Moreover, CO_2 sequestration at atmospheric pressure is enhanced up to 60°C curing/activation temperature. Above this temperature, the CO_2 reaction decreases [13]. The temperature can be applied by heating the gas before inflating it or placing the chamber inside an oven. The carbonation duration range from two hours to twenty-eight days in different studies and the property development increases with the carbonation duration [22]. Compacting the sample when moulding is important as it will be homogenous and can provide less porosity [61]. The curing process also changes in different studies. Some researchers test the samples right after the carbonation while others let it to air-curing up to thirty-five days [34]. Carbonation duration and compacting pressure are shown in Table 2. Some researchers have demonstrated that the utilisation of sodium chloride and sodium bicarbonate as additives can enhance the carbonation reaction when diluted in water [13].The carbonation setup used by Mahoutian et al. is shown in Figure 2.

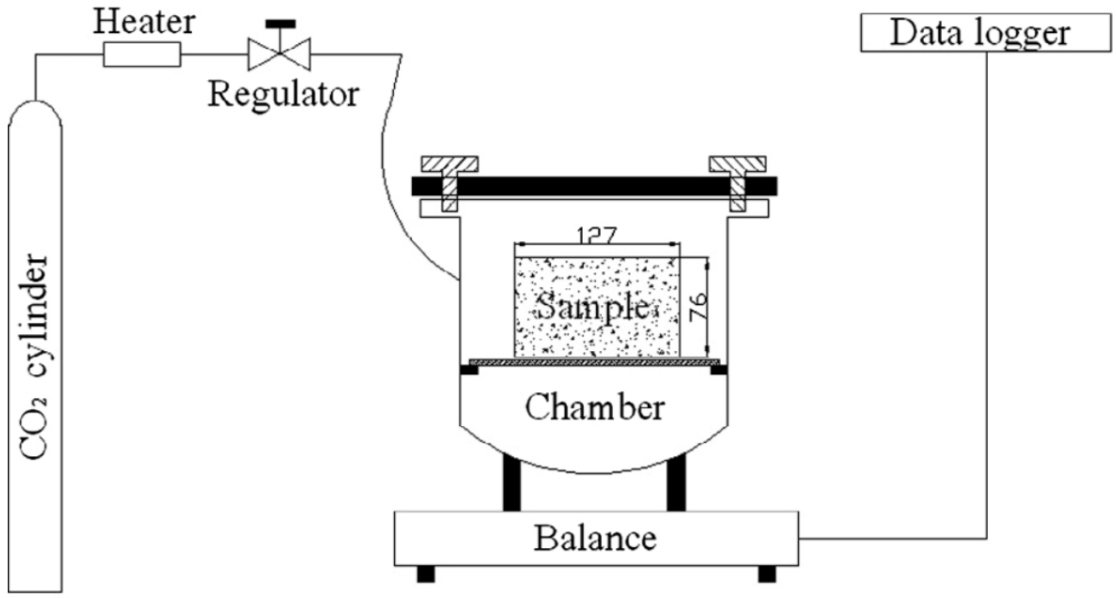

Figure 2 - Carbonation setup for carbon dioxide activated materials [34].

5. Steel Slag-Based Materials Activated by Carbonation

The steel slag-based materials activated by carbonation are produced by the combination of a grinded slag powder and water under the mentioned conditions and procedures. Besides being a cement-free construction material, they can store carbon dioxide and steel slag waste permanently. Among the carbon dioxide activated materials, studies about the binder have been increasing and there is plenty of information available about its mechanical properties and microstructure which confirm the binder capacity for structural applications. The binder is used as traditional Portland cement replacer for other applications which use natural and waste-based aggregates to produce different materials.

Mo et al. studied a carbon dioxide activated concrete which had as binding materials 60% of steel slag, 20% of Portland cement and 20% of reactive magnesia and lime. This concrete was neither cemented nor based on slag, yet it already showed the steel slag binder potential for concrete applications. Moreover, they used steel slag as aggregates which showed a better compressive strength development in comparison with the concrete that had natural aggregates. The higher compressive strength can be explained due to the carbonation of the steel slag which improved the interface between the aggregates and the binder matrix [38].

Mahoutian et al. developed another application which was the production of slag-based carbon dioxide activated masonry blocks. The blocks had only steel slag as a binder and granite as aggregate. A comparison with traditional cement masonry blocks showed that steel slag carbon dioxide activated masonry blocks have equal and sometimes better mechanical and durability

properties. Also, the leaching properties and fire resistance performance satisfied a reference document from the United States Environmental Protection Agency and ASTM standards respectively. Besides reducing carbon emissions and landfilled waste, slag-based block production was economically viable [15]. Mahoutian and Shao developed a concrete construction block made only with steel slag as binder and blast furnace slag as lightweight aggregates showing that carbon-negative and cement-free construction blocks can be economically competitive with the traditional cement block if produced in an industrial scale. Moreover, such blocks produce no waste, consume no natural resources and have better mechanical and durability properties [62].

There are further potential applications for slag-based carbon dioxide activated materials which can reduce to zero the steel slag landfills and reduce significantly the carbon dioxide emissions in a global perspective.

6. State of Current Research Results: Properties and Discussion

6.1. Compressive Strength

Ghouleh et al. achieved a compressive strength of 80.5 MPa after 2 hours of carbonation while Mahoutian et al. reached 39.5 MPa after 24 hours of carbonation, showing evidence of the non-linear behaviour and different compressive strength development depending on the material properties, carbonation conditions and mix design procedures. In some studies, the compressive strength was measured even without carbonating the sample aiming to discover if the mixture would harden just through hydration [63]. Such study achieved low compressive strength results representing the weak hydration reactivity of the steel slag. Moon and Choi have obtained up to 29.1 MPa compressive strength with only 5% of CO_2 concentration. However, they mixed 30% of Portland cement with steel slag and left it to cure for 28 days at a constant temperature and humidity [39]. Mahoutian et al. have done two steel slag panels with EAF and a mix of EAF and BOF steel slags using the same process and parameters. Both powders had quite similar chemical compositions, changing only its fineness where the EAF slag was coarser. The panel which had a mixture of steel slags displayed 78% higher compressive strength, showing that the steel slag fineness is a critical parameter regarding the material compressive strength development [25]. As mentioned before, comparing the achieved results from each other is not the best way, but the interpretation of each study helps to analyse that the compressive strength increases with the higher total pressure of the CO_2 gas [64], carbonation duration and with extra curing regardless the curing environment [21]. The highest compressive strength achieved in each study is shown in Table 3. Besides the 9 MPa case, results show that the steel slag-based carbon dioxide activated materials have good potential as a Portland cement replacer for precast applications.

6.2. Carbon Dioxide Uptake

Carbon dioxide uptake analysis as it was expected by the researchers followed the compressive strength behaviour. Samples with high compressive strength development showed higher CO_2 uptake [22]. The CO_2 uptake also increased due to carbonation duration. Two different mixtures left for 2 and 24 hours of carbonation showed an increase between 30-50% in the CO_2 uptake (Mahoutian et al., 2015). Siriwardena and Peethamparan have found for GGBFS a quite low CO_2 uptake ranging from 1.32-1.83%. They also found that by adding water, the CO_2 uptake amount increases. However, no compressive strength test was made and the used slag was as-received, not mentioning its fineness which can be a reason for such low uptake [32]. Some researchers have not measured this parameter. However, the highest CO_2 uptake achieved was 17.6% by mass [63] which represents an interesting value for reducing significantly the amount of CO_2 in the atmosphere and minimizing the global warming effects. Table 3 also shows the CO_2 uptake of the studies under review.

Table 3 - Compressive strength, CO_2, uptake, formed products and porosity of CO_2 activated materials.

Reference	Precursors	Higher Compressive Strength (MPa)	CO_2 Uptake (%)	Formed Products	Porosity
[22]	BOFS	110.6	0 - 13.22	C-S-H $CaCO_3$	
[37]	Steel Slag	9		$CaCO_3$	
[34]	Ladle Slag	39.5	4.0 - 12.8	C-S-H C-A-H $CaCO_3$	
[25]	EAF Slag	20.1	1.7 - 4.6	C-S-H $CaCO_3$ Ca(OH)	
	Mix of EAF Slag and BOF Slag	35.9	3.3 - 4.8	C-S-H $CaCO_3$ Ca(OH)	
[38]	Steel Slag	44.1	0 - 17.6	$CaCO_3$	15.7 - 33.6
[39]	Steel Slag	29.1	13 - 17	$CaCO_3$	34 - 38.3

[a] The range of values is compiled due to the same study uses of several blends or carbonation conditions

6.3. Microstructure

The microstructural analysis helps to characterize the pores and distinguish which were the formed and consumed products, besides analysing the binder and its composition in a good scale.

6.3.1. Pore Characterization

Only Mo et al. characterized the pores and found that with carbonation and consequently calcite ($CaCO_3$) production: total pore volume, maximum and average pore sizes reduced significantly which augment the compressive strength. Comparing a steel slag binder before and after carbonation, the non-carbonated sample has three times bigger coarse pore diameters and almost 50% more of total pore volume than a one-day carbonated sample. Moreover, comparing the non-carbonated sample with a fourteen days carbonated sample the coarse pore diameter can be reduced up to thirty times and the total pore volume by 2.5 times. [63]. Table 3 shows also the achieved range of porosity.

6.3.2. Formed Products

As it was expected from the reactions, all studies have found the production of the calcium carbonate $CaCO_3$ which gave the binders its binding properties, compressive strength, and porosity reduction. Moreover, some other products were also formed such as calcium silicate hydrate and calcium-aluminate-hydrate due to hydration [22]; carbonate-oxalate cancrinite group materials formed due to increasing of carbonation duration [71]; Magnesian calcite and nesquehonite that resulted from the carbonation of the combination of MgO and CaO [72]. Mahoutian has compared the thermogravimetric and differential thermogravimetric curves for three different curing conditions: 35 days of hydration, 24 hours of carbonation and 35 days of hydration after 24 hours of carbonation. Figure 3 evidenced that three different products were formed in different quantities depending on the carbonation conditions by the DTG peaks. The temperature range of 105-400°C represents the water loss of the first dehydration of calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH), which is quite similar in all the different conditions. The mass loss between 400-500ºC represents a water loss due to dehydration of Ca(OH) (CH), product of the reaction between steel slag and water which is not noticed on the only carbonation condition. The range of 500-900ºC represents the CO_2 loss due to decarbonisation of calcium carbonates. The only hydrated mixture showed no calcium carbonate formation, high amount of CH but not enough CSH formation for developing strong bonds on the paste, which evidences the low hydraulic behaviour of the steel slag. On the other hand, the high carbon dioxide reactivity was evident due to the calcium carbonate formation on both carbonated samples. Mo et al. have done SEM analysis and confirmed under a microscope scale a carbonated sample with calcite and calcium silicate hydrate

as products in the resulting binder, as shown in Figure 4. In Table 3 the formed products are mentioned [63].

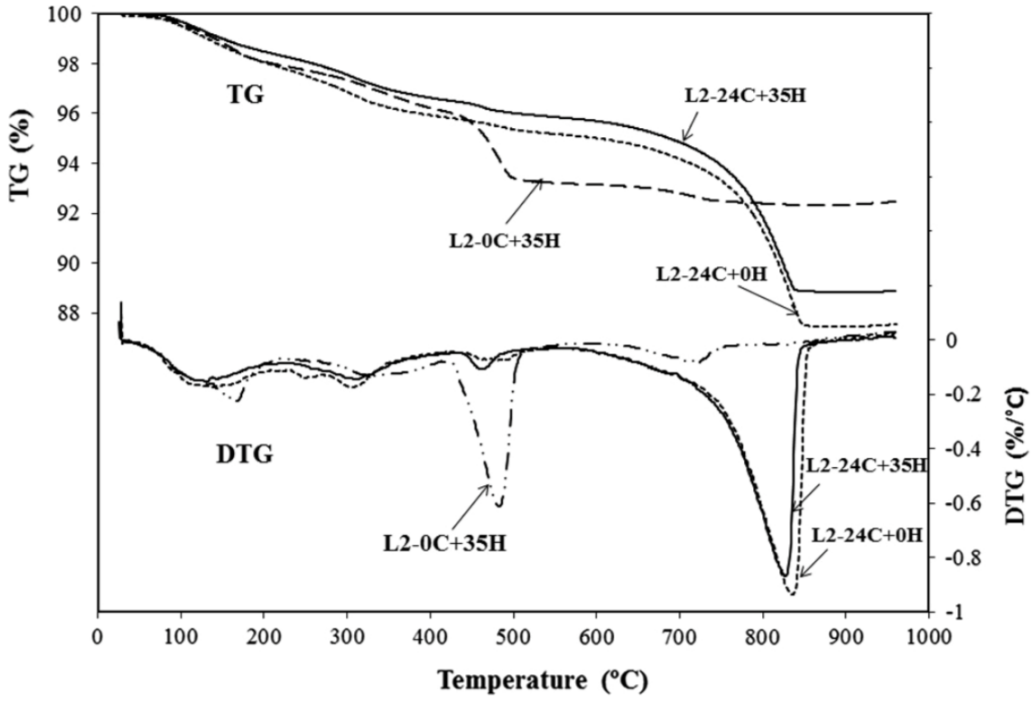

Figure 3 - Thermogravimetric and differential thermogravimetric curves of the steel slag binder (L2) after different curing conditions: 35 days of hydration (H), 24 hours of carbonation (C) and 35 days of hydration after 24 hours of carbonation (Mahoutian et al., 2014).

6.3.3. Mineralogical Phases

The mineralogical phases that are analysed through the X-ray diffraction also confirm the formation of some products. Furthermore, it shows the consumed phases which are mainly C_2S. However, some C_3S and mayenite ($C_{12}A_7$) were also consumed (Mahoutian et al., 2014). Ghouleh et al. also found that when the sample is hydrated before carbonation it is possible to see portlandite and some periclase (MgO) being consumed as well [22]. On the other hand, the X-ray diffraction analysis showed some phases that did not react under carbonation as the gehlenite and merwinite and apart from them, brownmillerite showed a low reactivity [63]. Figure 5 shows X-ray diffraction analyses comparing the mineralogical phase differences between the raw steel slag, only hydrated steel slag, and the carbonated plus hydrated sample, distinguishing the core and edge analysis individually. x γ-C_2S was mainly seen on the raw slag, which is a non-hydraulic calcium silicate, yet some β-C_2S namely a hydraulic calcium silicate was also found. When compared with the only hydrated sample, it is seen that only β-C_2S has

been consumed producing Ca(OH) which has no binding properties. On the other hand, the carbonated samples showed the γ-C_2S consumption beyond the β-C_2S, which originated the calcium carbonate production. As expected, the core has been less activated than the edge, once the edge has direct contact with the CO_2 rich atmosphere. Some non-reactive γ-C_2S was also found on the XRD analysis.

7. Recent Industry-related Developments

Science and industry have been working with the same goal, to reduce the carbon footprint by reducing CO_2 emissions on the concrete process. Besides producing some eco-friendly materials, these binders and concretes have also good mechanical properties.

Two patents from the United States of America refer to materials that after carbonating show good properties. In one, calcium-rich cementitious materials are carbonated, mixed with water and then used as an addition to produce concretes which have less CO_2 emissions on its process. One of the objectives is to reduce the CO_2 emissions on the concrete industry using this carbonated slurry as an addition which is made before the ordinary Portland cement, aggregates and further materials being mixed [65]. Additionally, the material is used as a bonding element or matrix on the core, first or seconding layer of the material structure. Even the system considered the material structure, it should be optimized, despite already having good mechanical, thermal, magnetic, optical and nuclear properties. Its method of manufacturing is also defined and described by other researchers[66]. As expected on the carbonated materials the main product of the reaction is calcite ($CaCO_3$) which provides mechanical property improvements to the final structure.

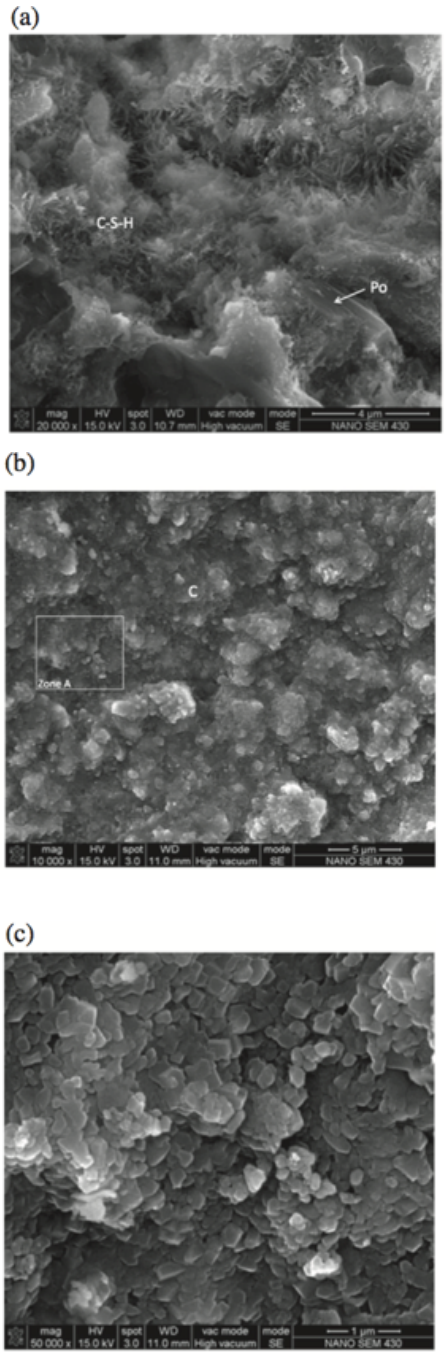

Figure 4 - SEM image of steel slag pastes before and after CO2 curing: (a) steel slag paste, before CO2 curing; (b) steel slag paste, after 14 d of CO2 curing; and (c) calcium carbonate formed in steel slag paste, closer look at Zone A in (b) [63].

The industry has followed science in order to try to reduce the carbon footprint through concrete manufacturing. Some companies developed ideas and process which produce cement-free binders or even supplementary cementitious materials to replace part of the cement on the traditional concrete mixes. Novacem is one of the companies which are used to produce a cement-free binder made with a magnesium oxide material that captures CO_2 when mixed with water in a CO_2 environment. The main product of Novacem's binder was magnesium carbonate which was responsible for its strength [67]. Solidia is another company that has a non-hydraulic cement that is activated by the reaction of CO_2 and calcium silicates under specific conditions. As expected, calcite and silica are the main products and those responsible for the strength and cracking resistance of the material. Solidia cement can reduce the carbon footprint of the concrete process by 70% and has casting conditions like standard ordinary Portland cement concretes [68]. Calera is another company which produces a calcium carbonate CO_2 activated binder system for concrete products. Its cement is free of any ordinary Portland cement and has higher compressive strength. Besides the binder system, the company also produces the calcium carbonate as a supplementary cementitious material that replaces around 15% of the Portland cement on the concrete mix [69]. The Carbon Cure is another company in this field which has a slightly different application, captured CO_2 from industrial processes are inflated into Portland cement with water. The carbonation is responsible for the increase between ten to twenty percent of the strength of the material, yet the final amount of CO_2 emission reduction is about five percent compared to a standard concrete ordinary Portland cement production [70].

These companies have shown how efficient and possible the carbon activated binders and concretes are based on their properties and CO_2 usage. However, this process is only limited to precast applications. The usage of many calcium and magnesium-rich wastes is the main challenge for further researches. Costs must be carefully analysed based on industrial-scale production plants as standards are needed to make the material reliable for society.

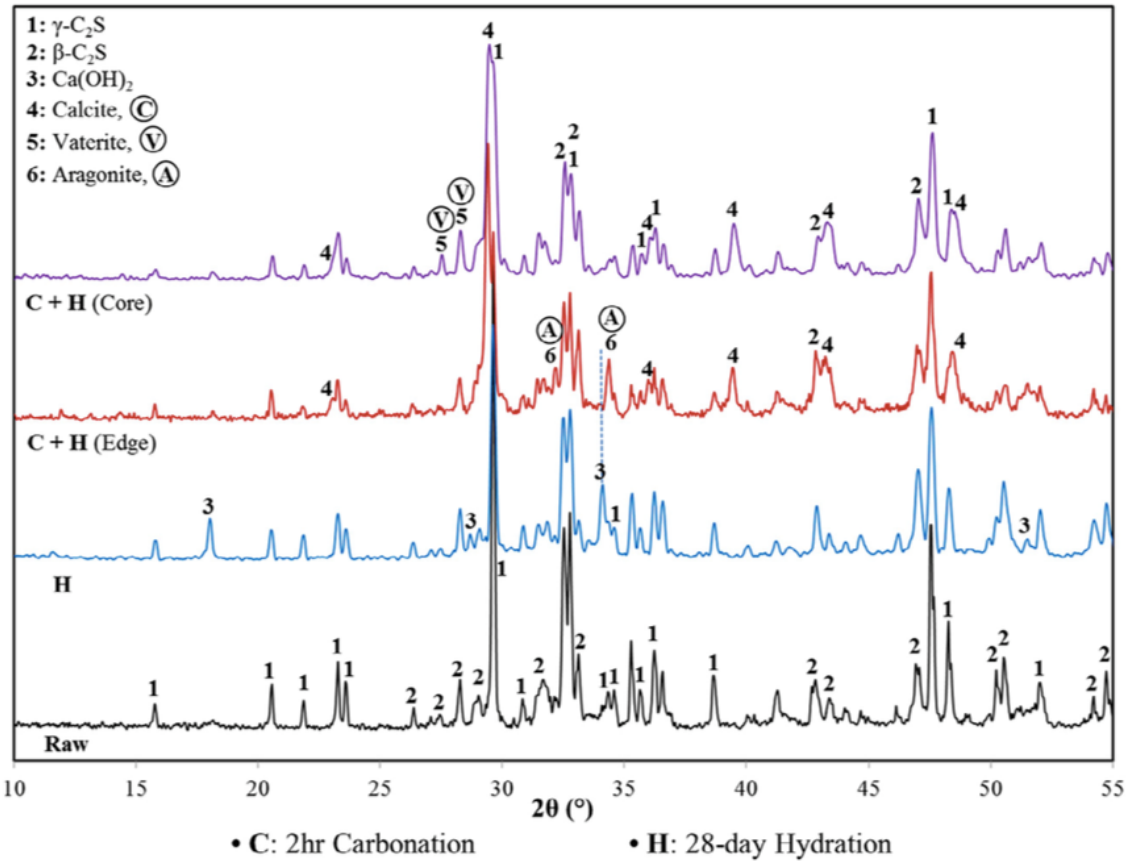

Figure 5 - XRD spectra from a steel slag comparing different curing scenarios with the raw material [22].

8. Research Needs and Industrial Feasibility Prospects

Further investigation can be done on pH, total pressure and relative humidity influence on the carbonation. Understanding the influence of these variables would help the comprehension of the binder behaviour and together with optimisation on carbonation and curing conditions it might improve the binder processing and properties. As the chemical composition of the used waste material can help or disturb the carbonation, investigation regarding proper additives can be done to support less reactive waste and increase the activation of the well-reactive materials.

Further research is also needed to enable the utilisation of this construction material in the market, particularly in the materials and construction sector. At first, few applications prototypes should be analysed to see how the fresh and hardened properties will behave. Therefore, the carbonation size effect needs to be efficient since the core and edge of the concrete must activate well to keep all properties proper for structural applications. Together with the size effect, data should be collected from all the properties that will be investigated since standardization and certification is important for producing and trading affairs.

Moreover, the cost analysis should be done along with an industrial scale production process design, so that it will be possible to evaluate in which technical application this construction material will be economically feasible. Life cycle analysis should be done and accounted for such as waste management and carbon credits to represent real economic efficiency of the slag-based materials activated by carbonation.

9. Conclusions

This review exposes a reasonable study with comparisons covering several topics about slag-based carbon dioxide activated construction materials. The following main conclusions can be drawn from this review:

- Steel slag carbonation is a chemical reaction, under controlled conditions, between different silicates and CO_2 that mainly produces carbonates with binding properties.
- The slag-based binders and materials activated by CO_2 are produced by the combination of a grinded slag powder and water.
- The chemical composition and fineness of the slag, the water content of the mixture, the concentration and total pressure of CO_2, the temperature of curing, the compacting pressure of the slag and carbonation duration are critical parameters for a reaction.
- Compressive strength development of CO_2 activated steel slag-based materials depends on precursors properties, carbonation conditions, and mixture design procedures which is an advantage due to different alternatives to improve its performance. Their compressive strength is suitable for precast building applications which can replace a large amount of ordinary Portland cement at the construction material industry.
- The carbon dioxide activated binder has a great potential to switch the way of an enormous amount of waste that would be landfilled, towards turning it into a building construction material that stores this waste permanently through an industrial scale of manufacturing this binder.
- The reduction of CO_2 content on the atmosphere has a great potential since manufacturing this binder can store up to 1.76 tons for every 10 tons of binder produced, and this ratio can be even improved with further studies reaching the optimal methods and conditions. Moreover, the difference between CO_2 emissions on the manufacturing process of Portland cement and the carbon dioxide activated binder should be measured to have a better comparison of the CO_2 reduction ratio. Therefore, the binder is a good solution to global warming.
- Nowadays the main barriers to using this technology on an industrial scale are the cost and lack of standards. These two situations are normal and expected because the slag-based binder activated by carbonation is a new material and has only a few on it.

Further research is needed on the pH, total pressure and relative humidity influence carbonation reaction. Additionally, a study on the feasibility of this construction material and the market needs, particularly in the materials and construction sector.

Acknowledgment

This work was partially supported by the Doctoral Incentive Grant BID/ICI-FE/Santander Universidades-UBI/2017 financed by the Santander-Totta bank and the University of Beira Interior.

This work was also partially financed by Portuguese national funds through FCT – Foundation for Science and Technology, IP, within the research unit C-MADE, Centre of Materials and Building Technologies (CIVE-Central Covilhã-4082), University of Beira Interior, Portugal.

Chapter 3
Experimental Procedure

1. Experimental Program

This work aims at studying a novel CO_2 activated EAF slag-based binder through the analysis of the influence of the sample preparation, carbonation conditions, additives and complementary curing on the binder compressive strength development. It aims at analysing and characterising CO_2 activated EAF slag-based binders with potential as Portland cement-based binders' replacers for precast building applications. The CO_2 activated binder consists of EAF slag which is calcium rich activated under a CO_2 rich controlled atmosphere.

The experimental program was divided into six distinct phases which were distributed temporally through the schedule presented at the end of this section. Processes parameters were manipulated aiming at reaching acceptable compressive strength as a Portland cement substitute for building material applications. EAF slag fineness, water to solid ratio, compacting pressure, System total pressure, oven temperature and carbonation duration were adjusted to achieve optimal results. Additives and complementary curing process were tested and had their effects discussed on the CO_2 activation. The combination of each parameter optimal condition was the binder's optimal condition. EAF slag and Portland cement sample were activated under the binder's optimal condition for comparison purposes.

An experimental program was carried out to analyse how the EAF slag cured under a 99.9% carbon dioxide atmosphere behaves with variations on the sample preparation, carbonation parameters, additives utilisation and complementary curing. The combination of all parameters which performed better was selected for optimal reaction conditions to activate the EAF slag-based binder. A comparison with Portland cement CEM II/B-L 32.5 N manufactured by Cimpor was also carried out. The changed parameters were slag fineness (f), water to solid ratio (w), compacting pressure (c), System total pressure (pp), oven temperature (T), carbonation duration (t), ethanol utilisation, sodium chloride utilisation, sodium bicarbonate utilisation, grinded glass utilisation, plastic bag curing before and after carbonation, moisture room curing before and after carbonation, underwater curing after carbonation, and oven curing after carbonation. However, when one parameter/condition was being manipulated, there was a fixed value for the others as standard carbonation condition. For the additive utilisation and complementary curing, a semi-optimal carbonation condition was used. A total of 150 samples were moulded and tested in 50 different conditions. An electric arc furnace slag was received from the National Steel Industry in Maia and Seixal, Portugal.

The EAF slag and Portland cement powders were characterised in order to gather all important information related to the powder reactivity with CO_2 and its basic characteristics.

2. Description

The experimental process was constituted by eight phases:

1) Chemical and mineralogical phase's analysis were done to identify the powders' compounds and mineralogical phases highlighting the CO_2 reactive and non-reactive. As indicated in Chapter 2, calcium-rich powders are more reactive to CO_2 where the most reactive mineralogical phase is ß-C_2S. In addition to the chemical properties, some physical properties were analysed in order to classify and compare the powders and analyse the feasibility application. Density, powder fineness and particle size analysis were done. As a potential substitution for building materials, the density comparison is pretty important in order to evaluate the main challenges of applying this material. The powder fineness and particle size analysis support the understanding of their influence on the reaction and its comparison with the Portland cement.
2) The EAF-slag as received was subjected to drying, milling, and grain size separation in order to be subjected to mixing and carbonation. The grinded and separated powder was mixed with water in three different ratios to analyse which would perform better under carbonation. After being mixed with water, the fresh mixture was moulded by compaction into cylindrical moulds under three different compaction pressures to verify the relationship between the applied compaction pressure and compressive strength development under CO_2 activation.
3) The compacted moulded samples were subjected to carbonation and the manipulation of the carbonation parameters was studied in order to analyse their influence on the binder's compressive strength development. The samples were subjected to four different temperatures, three different System total pressure and eight different curing durations.
4) The utilisation of additives was analysed dividing them into two subgroups: water modification additives or EAF slag partial replacer additives. Sodium chloride (NaCl) and sodium bicarbonate ($NaHCO_3$) were diluted in water, thus modifying the water characteristics, ethanol was mixed partially replacing the water and grinded glass was mixed partially replacing the EAF slag.
5) The carbonated samples were subjected to a complementary curing method to analyse if there was any positive or negative effect in realizing the few different complementary curing conditions. The carbonated samples were subjected to a plastic bag and a moisture room before, after or before and after carbonation; as were subjected to an oven or put underwater after carbonation. Each plastic bag, moisture room, and the underwater cycle was of seven days and the oven curing cycle was from zero to three days.

6) Two extra conditions were applied on this study letting the fresh sample in a plastic bag or a moisture room for seven days to analyse the hydration potential of the EAF slag samples to evaluate their compressive strength development through hydration.
7) All hardened samples were tested in order to evaluate its performance and synthesize the information. All hardened samples were subject to a compressive strength analysis. Few specific samples were subjected to further tests such as X-ray diffraction analysis, scanning electron microscope analysis, back-scattered electron detector analysis and thermogravimetric analysis in order to evaluate the consumed and formed mineralogical phases, formed products, microstructure, and carbonation degree.
8) All the results were analysed and discussed.

Chapter 4
Materials and Methods

1. Preliminary Information

An electric arc furnace (EAF) slag was received from the National Steel Industry in Maia and Seixal, Portugal where it is currently being used to replace aggregates in few construction applications such as compacted soils, pavements base, sub-base and floor bed, parking lots, landfills, gardens and green areas, train lines, and football fields [73]. Previous researchers have studied the National Steel Industry EAF slag utilization for alkaline activation [74] but the presented work is the first which evidences its utilization as a unique binder material activated by accelerated carbonation curing. Two different EAF slag fineness were used over the research work and both powders were characterised, those which are mentioned as Slag 45 and Slag 125, once each powder passed 100% through the sieves 45 μm and 125 μm respectively.
The studied parameters were slag fineness (f), water to solid ratio (w), compacting pressure (c), System total pressure (pp), oven temperature (T), carbonation duration (t), ethanol utilisation, sodium chloride utilisation, sodium bicarbonate utilisation, grinded glass utilisation, plastic bag curing before and after carbonation, moisture room curing before carbonation, moisture room curing before and after carbonation, underwater curing after carbonation, oven curing after carbonation. A total of 150 samples were moulded and tested in 50 different conditions. A standard condition of 529 m^2/kg (f), 10% (w), 30 MPa (c), 1.5 bar (pp), 40 ºC (T), 24 h (t), no additives; and one day of oven curing after carbonation. The chosen optimal conditions to be compared with Portland cement were 529 m^2/kg (f), 10% (w), 30 MPa (c), 3.5 bar (pp), 60 ºC (T), 24 h (t), no additives, and one day of oven curing after carbonation. Table 4 evidences all carbonation conditions performed at the experimental program, highlighting the standard and optimal conditions, Table 5 evidences the conditions related with the additive utilization, and Table 6 evidences the conditions related with the complementary curing.

Table 4 - Carbonation conditions

Changed Parameters		Fineness (m^2/kg)	Water to Solid (%)	Compacting Pressure (MPa)	Temperature (ºC)	Total Pressure (bar)	Duration (h)
Standard		529	10.0	30	40	1.5	24
Fineness	f1*	529	10.0	30	40	1.5	24
	f2	136	10.0	30	40	1.5	24
Water to solid	w1*	529	10.0	30	40	1.5	24
	w2	529	12.5	30	40	1.5	24
		529	12.5	30	50	1.5	24
		529	12.5	30	60	1.5	24
		529	12.5	30	70	1.5	24
	w3	529	15.0	30	40	1.5	24
		529	15.0	30	50	1.5	24
		529	15.0	30	60	1.5	24
		529	15.0	30	70	1.5	24
Compacting pressure	c1	529	10.0	10	40	1.5	24
	c2	529	10.0	20	40	1.5	24
	c3*	529	10.0	30	40	1.5	24
Temperature	T1*	529	10.0	30	40	1.5	24
	T2	529	10.0	30	50	1.5	24
	T3	529	10.0	30	60	1.5	24
	T4	529	10.0	30	70	1.5	24
Total pressure	pp1*	529	10.0	30	40	1.5	24
	pp2	529	10.0	30	40	2.5	24
	pp3	529	10.0	30	40	3.5	24
Carbonation duration	t1	529	10.0	30	40	1.5	0.5
	t2	529	10.0	30	40	1.5	2
	t3	529	10.0	30	40	1.5	4
	t4	529	10.0	30	40	1.5	8
	t5	529	10.0	30	40	1.5	12
	t6*	529	10.0	30	40	1.5	24
	t7	529	10.0	30	40	1.5	48
	t8	529	10.0	30	40	1.5	72
Optimal		529	10.0	30	60	3.5	24

* Carbonation conditions are the same as the standard carbonation conditions

Table 5 - Additive utilization

Additive		Condition
Ethanol (water replacement %)	E10	10
	E20	20
	E30	30
NaCl (concentration in water g/L)	NC1	10
	NC2	20
	NC3	30
$NaHCO_3$ (concentration in water mg/L)	NH1	100
	NH2	200
	NH3	300
Glass waste (slag replacement %)	G05	5
	G10	10
	G15	15

Table 6 - Complementary curing

Before Carbonation (days)			CO_2 Curing (days)	After Carbonation (days)			
Condition	Sealed Bag	Moisture Room		Oven	Sealed Bag	Moisture room	Underwater
UA	0	0	1	1	0	0	1
SB1	7	0	0	0	0	0	0
SB2	7	0	1	1	0	0	0
SB3	0	0	1	1	7	0	0
SB4	7	0	1	1	7	0	0
MR1	0	7	0	0	0	0	0
MR2	0	7	1	1	0	0	0
MR3	0	0	1	1	0	7	0
MR4	0	7	1	1	0	7	0
OV0	0	0	1	0	0	0	0
OV1	0	0	1	1	0	0	0
OV2	0	0	1	2	0	0	0
OV3	0	0	1	3	0	0	0

2. Steel Lag and Portland Cement Characterisation

2.1. Chemical Analysis

The chemical compositions of the EAF slag and Portland cement were determined by energy dispersive spectroscopy (EDS) analysis. Through the analysis, it was possible to see that the slag is right in calcium (CaO), iron (Fe_2O_3) and silica (SiO_2) with some other minor oxides in its composition and the Portland cement being also rich in calcium (CaO) and silica (SiO_2) with some other minor oxides in its composition including iron (Fe_2O_3). Chemical compositions from steel slag and Portland cement are shown in Table 7. EDS analysis was done by using a Hitachi S-4800 scanning electron microscope. The microscope was operated at a 15 kV at a working distance from 7.1 mm. The specimens were examined for EDS using a Bruker Xflash 5010 Cooled with a Peltier resolution ≤ 129 eV of Mn.

Table 7 - Powders characterisation

Material	Oxides percentage by mass						Density (g/cm^3)	Blaine number (m^2/kg)
	CaO	SiO_2	Al_2O_3	MgO	SO_3	Fe_2O_3		
Slag 45	30.21	14.18	12.00	5.58		29.51	3.771	529
Slag 125	30.91	13.67	10.74	4.65		28.27	3.703	136
OPC	62.20	12.31	3.08	1.27	4.33	2.42	2.977	382

2.2. Mineralogical Properties

The mineralogical properties of the EAF slag and Portland cement were performed through X-ray diffraction (XRD) analysis. The powders were analysed with a Rigaku DMAX III/C instrument equipped with Cu (Kα) X-ray tube which made a 5-90° 2θ scan at an operation voltage of 40 kV and a current of 30 mA, evidencing the mineralogical phases of each powder.

The Slag 45 and Slag 125 evidenced similar and four main mineralogical phases which were Gehlenite, Wusite, Alite (C_3S) and Belite (C_2S). In terms of carbon dioxide reactivity, researchers indicated that Gehlenite and Wusite do not react at all under carbonation while C_2S is the most CO_2 reactive phase, especially when it is ß-C_2S, the C_3S has lower carbonation reactivity when compared to C_2S, thus being more reactive with water [34,58,63].

The Portland cement did not evidence any trace of iron-rich phases over the XRD analysis highlighting mainly C_3S and C_2S where the amount of C_3S is much greater which was expectable due to the Portland cement reactivity with water and it is a traditional and common application where Portland cement artefacts get hardened by hydration.

2.3. Density

The EAF slag and the Portland cement were subjected to a density test using a gas displacement pycnometer (AccuPyc1340, Micrometrics, Norcross, Georgia). The Slag 45 presented a slightly higher density when compared with the Slag 125 and both EAF slag had its density higher than the Portland cement. Results are shown in Table 7.

2.4. Fineness

The EAF slag and the Portland cement had their fineness characterisation made through a Blaine test according to EN 196-6 using ACMEL LABO BSA1 apparatus. The fineness results represented what was expected to evidence: greater Blaine number to the Slag 45, 529 m^2/kg when compared with the Slag 125, 136 m^2/kg, the Portland cement fitness was in between both powders, 382 m^2/kg, but much closer to Slag 45. Micrographs of the two different EAF slag powders are shown in Figure 6 to represent the grain size difference.

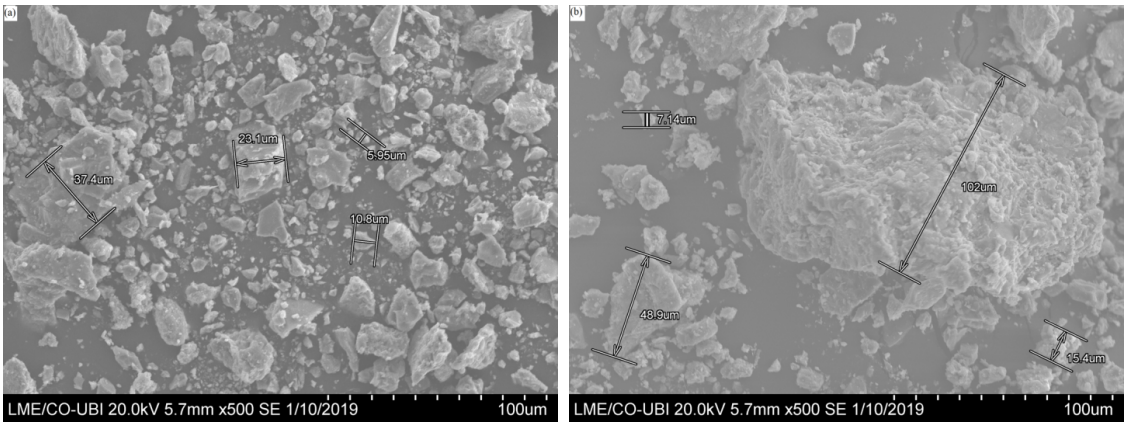

Figure 6 - Micrographs of the 45µm (a) and 125µm (b) steel slag powders before carbonation.

2.5. Particle Size Analysis

The EAF slag and the Portland cement were subjected to a particle size distribution determination by laser diffraction (CILAS, 1190) which behaved in accordance with the powders' fineness and is evidenced in Figure 7.

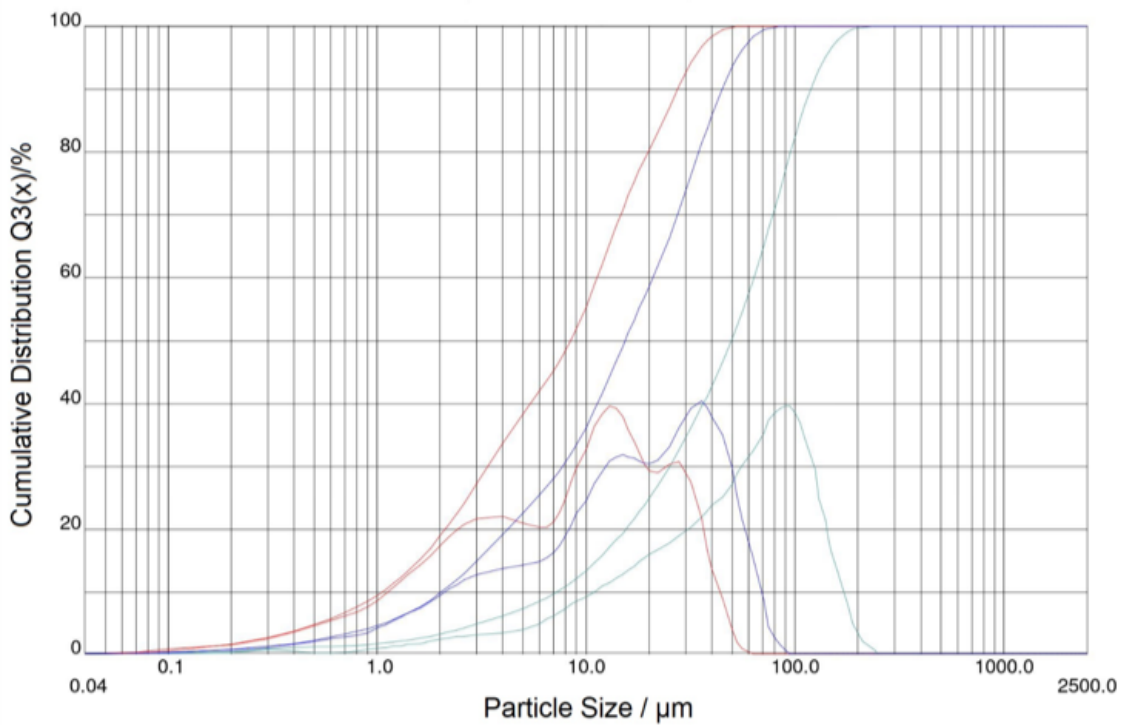

Figure 7 - Particle size distribution: cumulative and volume fraction of slag 45 (red), slag 125 (green) and Portland cement (blue).

3. Sample Preparation

3.1. Drying, Milling and Grain Size Separation

An EAF slag received from the National Steel Industry was placed as received in the oven at 60ºC for 24 h to dry. This process was done in order to improve the milling phase by reducing the possibility of agglutination of the fine powders which could slow down the milling process and request an extra phase before the grain size separation since agglutinated grains would not pass over the sieve correctly.

After drying, the EAF slag was first subjected to a crusher mill in order to be grinded into a small size. This grinding process had an energy consumption of 12 kWh per ton of steel slag crushed. After being grinded, in order to pulverize the EAF slag powder to grain sizes under 45 µm and 125 µm, the EAF slag powder was subjected to a ball mill. The pulverizing process had an energy consumption of 12.5 kWh and 37.5 kWh per ton of coarser and thinner steel slag powder respectively.

After pulverizing, each EAF slag powder was sieved into 45 µm sieve and 125 µm sieve in order to assure that no particle size over the desired maximum dimension was present in the batch.

3.2. Mixing: the Water to Solid Ratio

Each EAF slag, the Slag 45 and the Slag 125, were mixed with three different water to solid ratio always calculated by weight. Each mixture was made with 100g of EAF slag powder plus water depending on the specific water to solid ratio. For each mixture, three samples were further moulded and compacted. The used water to solid ratio was 10.0%, 12.5%, and 15.0%.

3.3. Compacting and Fresh Samples Porosity

After mixing with water, the mixture was poured into a cylindrical mould of 20 mm of diameter and 60 mm of height and compacted with a 3000 kN electro-hydraulic mechanical testing machine (ADR Touch 3000 BS EN Compression Machine with Digital Readout and Self Centring Platens) in accordance with EN 196-1 under three different compacting pressures 10, 20 and 30 MPa. Fresh samples had 20 mm of diameter and 40 ± 05 mm of height.
Fresh samples of the slag 45 had their porosity (η) calculated as a function of initial slag moulded specimens' weight and volume:

$$\eta = 1 - \gamma_s/\gamma_p \times 100 \quad (1)$$

Where γ_s is the bulk density of the specimen to be tested and γ_p is the particle density of the steel slag. The samples were subjected to carbonation activation immediately after being moulded under compaction.

4. Curing Conditions

4.1. Oven Temperature

The fresh moulded samples were placed into the carbonation chamber which was inside an oven. The oven was already working with the desirable steady temperature. Four different temperatures were studied, 40ºC, 50ºC, 60ºC, and 70ºC in order to find the optimal temperature that would enhance the CO_2 activation to reach higher compressive strength development.
The carbonation chamber was at room temperature (17.5 ± 0.2 ºC) and had its temperature increase inside the chamber measured with HygroLog HL-NT3-DP. For each studied temperature, before placing it into the oven. The data was recorded in periods of five minutes in order to register the temperature balance between the chamber and the oven. The temperature of the oven was similar to the temperature inside the chamber after 40, 50, 55 and 60 min when the oven was at 40ºC, 50ºC, 60ºC, and 70ºC respectively. The chamber temperature increase is shown in Figure 8.

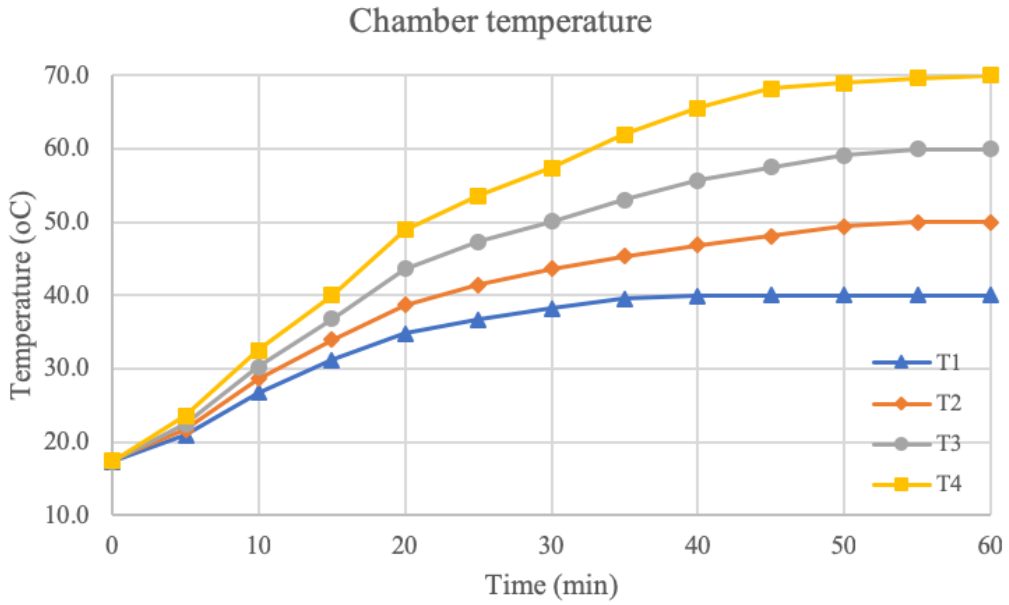

Figure 8 - Chamber temperature increase.

4.2. Carbon Dioxide Total Pressure

After placing the samples inside the chamber, locking it, and placing the chamber inside the oven, CO_2 was injected inside the chamber with 1.5 bar of total pressure. Then a top valve was open in order to release the current atmospheric from the chamber and then CO_2 was injected again to reach the experimental total pressure. Three different System total pressure were applied during the research work at 1.5 bar, 2.5 bar, and 3.5 bar. The CO_2 flow remained fixed at the desired total pressure in order to replenish the consumed CO_2 from the sample under carbonation. Each test had only three samples inside the carbonation chamber at the same time.

4.3. Carbonation Duration

After injecting CO_2, the samples were subjected to carbonation for eight different established periods, 0.5, 2, 4, 8, 12, 24, 48 and 72hrs. After the carbonation, samples were taken from the chamber to dry in an oven for 20hrs at 40ºC of temperature and then subjected to several different analysis right after the drying period.

5. Additives Utilisation

5.1. Current Additives for General Carbonation

Once the carbonation approach as a curing method is new, there are not many types of research conducted regarding the additive influence and utilisation for enhancing the reaction itself. Aiming at increasing the carbon dioxide sequestration in concrete, Haselbach and Thomle have investigated the influence of adding sodium bicarbonate in different concentrations to simulate water from the rivers and evaluate if the concrete carbonation would increase in comparison with average carbonation only exposed to the air. They have observed that increasing the sodium bicarbonate concentration the pH of the concrete samples has decreased faster what may represent an increase in the carbonation rate [10]. In a similar approach, researchers from the Korea University have investigated the influence of sodium chloride (NaCl) on the carbonation of concrete varying the NaCl concentration in water and also evaluating the pH behaviour during the experiment. The research evidenced that the calcium carbonates formation increased up to 18.4%, whereas the CSH formation decreased up to 33.0% revealing that the carbonation was enhanced with the NaCl utilisation [11]. However, both studies have analysed the additive utilisation for carbonating hardened concrete samples. In this thesis, the additive utilisation was conducted to understand the influence of potential additives to enhance the carbonation curing of steel slag-based binder. Besides using sodium chloride, sodium bicarbonate, and ethanol, due to its carbon content and high volatility, were used as water modification additives. Moreover, glass waste has been used as a steel slag replacer to evaluate if its high silica content would enhance the reaction.

5.2. Water Modification Additives

Three different additives were partially tested by replacing or being dissolved in water. The water modification and replacement were done before mixing with the EAF slag. Ethanol, Sodium Chloride (NaCl) and Sodium Bicarbonate ($NaHCO_3$) were used to partially replace or modify the water composition. Ethanol (96%) replaced 10%, 20% and 30% of water, NaCl was dissolved in water in the concentrations of 10 g/L, 20 g/L and 30 g/L, while $NaHCO_3$ was dissolved in water in the concentrations of 100 mg/L, 200 mg/L, and 300 mg/L. All samples which had water modification additives were only prepared using Slag 45, with 10% water to solid ratio, 30 MPa of compacting pressure and subjected to carbonation under 60ºC, with a System total pressure of 1.5 bar for 24hrs.

5.3. EAF Slag Replacement Additive

One additive was partially tested by replacing the EAF slag. The replacement was done before mixing the EAF slag with water. Glass waste collected from a local restaurant in Covilhã was grinded with a crusher mill and replaced in 5%, 10%, and 15%. The samples that had EAF slag replacement additive were only prepared using Slag 45, with 10% water to solid ratio, 30 MPa of compacting pressure and subjected to carbonation under 60ºC, with a System total pressure of 1.5 bar for 24 hrs.

6. Complementary Curing

6.1. Preliminary Information

The hydration degree and consequently compressive strength development of Portland cement-based binders and building materials after 24hrs of curing still under 50%, reaching 80% only after at least seven days (168 h) of curing which generally happens by exposition to environmental air [75,76]. The complementary curing study on this work is due to analysing if EAF slag after 24hrs of carbonation can still develop any compressive strength due to different types of curing methods or if there is any implication in preliminary curing before the carbon dioxide activation. This work presents an analysis of four different complementary curing methods which are underwater curing, moisture room curing, plastic bag curing, and oven curing. An extra condition was analysed without any complementary curing or drying step to evaluate if the drying step had any influence on the compressive strength development.

6.2. Underwater Curing

The underwater curing process was performed in order to observe if, after 24hrs of carbonation curing, the carbonated samples could still have any hydration or compressive strength gain by being underwater for 7 days.

6.3. Moisture Room and Plastic Bag Curing

The moisture room and plastic bag curing had the same approach, both aimed at analysing if the EAF slag samples could have any increase of compressive strength development by being cured under moisture room or plastic bag for 7 to 14 days. Moreover, the EAF slag was also subjected to moisture room and plastic bag curing to see the compressive strength development of the samples only by hydration for 7 days. As complementary curing methods, there were three different approaches: 7 days of complementary curing plus 24hrs of carbonation, 24hrs of carbonation plus 7 days of complementary curing, and 7 days of complementary curing plus

24hrs of carbonation plus 7 other days of complementary curing as described on Table 6 in the experimental program.

6.4. Oven Curing

The oven curing process was performed in order to observe if, after 24hrs of carbonation curing, the carbonated samples could still have any compressive strength gain for being under the temperature. The EAF slag carbonated samples were subjected to oven curing between zero to three days inside an oven at a temperature of 60ºC.

7. Carbonated Binders Characterisation

7.1. Compressive Strength

Carbonated binders were tested immediately after drying for compressive strength with a 3000 kN electro-hydraulic mechanical testing machine (ADR Touch 3000 BS EN Compression Machine with Digital Readout and Self Centring Platens) in accordance with EN 196-1 at a rate of 0.5 kN/s.

7.2. Mineralogical Characterisation

The X-ray diffraction (XRD) analysis was chosen to analyse the carbonation reaction, as well as consumed and formed products. Crushed samples from the EAF slag and Portland cement were analysed with a Rigaku DMAX III/C instrument equipped with Cu (Kα) X-ray tube which made a 5-90º 2θ scan at an operation voltage of 40 kV and a current of 30 mA. A comparative analysis was performed with the non-carbonated results in order to identify mineral logical phases consumed and produced during carbonation. The XRD analysis was carried out on the non-carbonated samples and the smashed carbonated samples of EAF slag and Portland cement. Ground samples represented the surface and the inner part of the activated binder.

7.3. Microstructure Characterization

A scanning electron microscope (SEM) analysis and back-scattered electron detector (BSE) analysis were performed. Two different microstructural analyses were carried out on the EAF slag and Portland cement. First, a cleaned small fractured piece of the carbonated binder was coated with gold to improve the imaging of the sample at the scanning electron microscope (SEM) analysis where the formed products could be seen. A small piece of each sample was cut, mounted to the stub with a resin, left to dry, then grinded and polished to go under the back-scattered electron detector (BSE). This sample was coated with carbon to improve the imaging

process and a section of the hardened sample was seen and analysed. The microstructural analysis was performed to see and compare product formation and structures. SEM and BSE analysis were done using a Hitachi S-4800 scanning electron microscope. The microscope was operated at a 15 kV at a working distance from 7.1 mm.

7.4. Carbonation Degree

Portland cement and EAF slag were subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using SHIMADZU TG-50 and DSC-50 apparatus, respectively. The TGA and DSC were performed to evaluate the formed products and compare with the before and after carbonation in order to calculate the carbonation degree by applying the methodology Tonoli et al. have done at their work [77]. The tests were carried out under N_2 flow (20 mL min^{-1}) at a heating rate of 20°C min^{-1}. The carbonation degree was calculated by comparing the difference between the quantity of CO_2 before and after carbonation [78]:

$$Dc(\%) = [(C-C_0)/C_{max}-C_0)] \times 100 \qquad (2)$$

Where C, C_0, and C_{max} are the amounts of combined carbon dioxide in a sample which was determined through the weight loss evaluation between 850-1000°C, ignoring the calcium carbonates that were already in the sample before carbonation. The C_{max} is the theoretical extent of carbonation [52]:

$$C_{max} = 0.785(\%CaO - 0.56\ x\%CaCO_3 - 0.7\ x\%SO_3) + 1.091\ x\%MgO + 0.71\ x\%Na_2O + 0.468(\%K_2O - 0.632\ x\%KCl) \qquad (3)$$

This is the maximum theoretical quantity of CO_2 required to react with the total calcium oxide (CaO) to produce calcium carbonates ($CaCO_3$).

Chapter 5
Results and Discussion

1. Compressive Strength Development

Compressive strength development was strongly influenced by the adjustment of studied parameters. Table 8, 9 and 10 shows the compressive strength results of EAF slag binder under all studied conditions.

Table 8 - Additive utilization' compressive strength

Additive		Condition	Compressive Strength (MPa)
Ethanol (water replacement %)	E10	10	75.8
	E20	20	69.5
	E30	30	51.7
NaCl (concentration in water g/L)	NC1	10	60.9
	NC2	20	71.4
	NC3	30	67.4
$NaHCO_3$ (concentration in water mg/L)	NH1	100	73.8
	NH2	200	62.6
	NH3	300	64.1
Glass waste (slag replacement %)	G05	5	66.3
	G10	10	57.4
	G15	15	41.8

Table 9 – Carbonation conditions' compressive strength

Changed Parameters		Fineness (m^2/kg)	Water to Solid (%)	Compacting Pressure (MPa)	Temper-ature (ºC)	Total Pressure (bar)	Duration (h)	Compressive Strength (MPa)
Standard		529	10.0	30	40	1.5	24	72.1
Fineness	F1*	529	10.0	30	40	24	24	72.1
	F2	136	10.0	30	40	24	24	28.8
Water to Solid	W1*	529	10.0	30	40	24	24	72.1
	W2	529	12.5	30	40	24	24	56.5
		529	12.5	30	50	24	24	60.0
		529	12.5	30	60	24	24	64.4
		529	12.5	30	70	24	24	57.4
	W3	529	15.0	30	40	24	24	49.0
		529	15.0	30	50	24	24	55.7
		529	15.0	30	60	24	24	61.2
		529	15.0	30	70	24	24	46.8
Compacting Pressure	C1	529	10.0	10	40	24	24	45.6
	C2	529	10.0	20	40	24	24	70.7
	C3*	529	10.0	30	40	24	24	72.1
Temperature	T1*	529	10.0	30	40	24	24	72.1
	T2	529	10.0	30	50	24	24	74.6
	T3	529	10.0	30	60	24	24	97.4
	T4	529	10.0	30	70	24	24	58.0
Total Pressure	Pp1*	529	10.0	30	40	24	24	72.1
	Pp2	529	10.0	30	40	24	24	126.6
	Pp3	529	10.0	30	40	24	24	128.1
Carbonation Duration	T1	529	10.0	30	40	0.5	0.5	12.5
	T2	529	10.0	30	40	2	2	26.7
	T3	529	10.0	30	40	4	4	37.5
	T4	529	10.0	30	40	8	8	55.8
	T5	529	10.0	30	40	12	12	60.8
	T6*	529	10.0	30	40	24	24	72.1
	T7	529	10.0	30	40	48	48	78.3
	T8	529	10.0	30	40	72	72	82.7
Optimal Slag		529	10.0	30	60	3.5	24	151.5
Optimal Cement		382	10.0	30	60	3.5	24	86.0

* Carbonation conditions are the same as the standard carbonation conditions

Table 10 - Complementary curing' compressive strength

Before carbonation (days)			CO_2 Curing (days)	After carbonation (days)				Compressive Strength (MPa)
Condition	Sealed Bag	Moisture Room		Oven	Sealed bag	Moisture room	Underwater	
UA	0	0	1	1	0	0	1	67.5
SB1	7	0	0	0	0	0	0	2.0
SB2	7	0	1	1	0	0	0	69.4
SB3	0	0	1	1	7	0	0	72.1
SB4	7	0	1	1	7	0	0	69.0
MR1	0	7	0	0	0	0	0	1.9
MR2	0	7	1	1	0	0	0	65.3
MR3	0	0	1	1	0	7	0	72.8
MR4	0	7	1	1	0	7	0	65.1
OV0	0	0	1	0	0	0	0	72.2
OV1	0	0	1	1	0	0	0	71.4
OV2	0	0	1	2	0	0	0	72.9
OV3	0	0	1	3	0	0	0	72.1

1.1. Sample Preparation

The EAF slag fineness results show that coarser powder has less activation due to their lower surface area; Blaine fineness represents the surface area difference from both powders. The coarser EAF slag powder (Slag 125) had three times lower compressive strength when compared with the finest EAF slag powder (Slag 45).

The water to solid ratio results showed that increasing the ratio over 10% the compressive strength development weakens. However, all analysed water to solid ratio evidenced good compressive strength development that can be applied for most of the building materials applications. The compressive strength of the samples with 15% water to solid ratio was lower in 32-37% in comparison with the 10% water to solid ratio samples but performed at no under than 46 MPa. The compacting pressure demonstrated that the more compacted the samples were before carbonating, the higher the compressive strength development since it provides less porosity as shown in Table 11 where a relationship between the water to solid, compact pressure and porosity is demonstrated. However, after 20 MPa of compacting pressure, there is no significant increase, only 1.98% of compressive strength increased from 20 to 30 MPa of compacting pressure.

Table 11 - Compacting pressure and porosity relationship

Sample	w (%)	c (MPa)	Porosity - η (%)
S11	10.0	10	46
S12	10.0	20	44
S13	10.0	30	36
S21	12.5	10	46
S22	12.5	20	40
S23	12.5	30	37
S31	15.0	10	42
S32	15.0	20	39
S33	15.0	30	37

1.2. Carbonation Conditions

The System total pressure evidenced a compressive strength increase when the total pressure was higher. The pressure improves the CO_2 diffusion, allowing higher carbonation of the samples. There is a great increase of 75% on the compressive strength development from 1.5 to 2.5 bar. However, between 2.5 and 3.5 bar, the compressive strength increased only 1.19%. The oven temperature manipulation showed that at 60ºC was the optimal result for the development of the compressive strength, since the temperature enhances the carbonation reaction. The compressive strength development related to the temperature manipulation is not linear evidencing only 3% of compressive strength gain from 40 to 50ºC while from 50 to 60ºC the increase in compressive strength is about 30%. However, over 60ºC, the carbonation reaction reduces due to faster water evaporation, which causes less CO_2 diffusion and evidences a lower final compressive strength development when compared with the other temperatures. The carbonation duration showed that the binder kept developing its compressive strength within the time progressively showing higher compressive strength with 72 hrs of carbonation. After only half an hour, the carbonated binder is already hardened with 12.5 MPa of compressive strength and after only one-two hours, the carbonated binder already evidences over 25 MPa.

1.3. Additives Utilisation

The additives utilisation did not evidence any significant compressive strength gain for the carbonated binders. Only the sample that had 10% of ethanol-water replacement evidenced a compressive strength increase which was about 6%. The ethanol-water replacement evidenced no negative influence on the compressive strength development up to 20% of the replacement. The sample with 30% ethanol-water replacement had 32% lower compressive strength compared

with the 10% ethanol-water replacement sample. This decrease on the carbonation reaction is also related to the fact that the CO_2 has lower solubility in ethanol compared to the one in water [79].

The NaCl dissolved in water did not evidence any significant compressive strength gain or loss. The lowest compressive strength was with the dissolution of 10 g/L of NaCl in water which evidenced a compressive strength of 83.40 MPa, 15% lower than the 20 g/L dissolution which had a compressive strength of 97.73 MPa similar to the 97.4 MPa which was the one used for comparison purposes. NaCl concentration in the Atlantic seawater is approximately 30 g/L and this results in the feasibility of using seawater for CO_2 activation of EAF slag based building materials without harming the compressive strength development [80].

The $NaHCO_3$ dissolved in water also did not evidence any compressive strength gain at all. Its loss was increasing with the $NaHCO_3$ concentration with 100 mg/L of concentration and the compressive strength was about 11% lower, while with 300 mg/L of concentration and the compressive strength was about 33% lower than the water without any additives under the same conditions.

The partial substitution of grinded glass did not evidence any compressive strength gain but a significant loss increased a lot after 10% of glass-EAF slag replacement. With only 5% of replacement, the compressive strength was only 7% lower but with 15% of glass-EAF slag replacement, the compressive strength was 41% lower compared with the 100% EAF slag sample under the same conditions.

1.4. Complementary Curing

The complementary curing study evidenced that the compressive strength development due hydration is not significant reaching only 1.9 MPa and 2.0 MPa for moisture room and plastic bag, respectively. When the complementary curing was performed before the CO_2 activation, the compressive strength results were about 13% and 30% lower for sealed bag and moisture room, respectively, when compared with samples which were subjected to carbonation immediately after being moulded. These results can support a design plan for a potentially industrial scale application where the building materials production is greater than the carbonation capacity and storage simulating a plastic bag for fresh samples waiting for carbonation would be more efficient than storing them in a moisture room.

For complementary curing, after the sample was subjected to carbonation, any compressive strength increase was evidenced. Compressive strength results varied less than 5% when the samples with complementary curing after carbonation, no complementary curing and with no drying step were compared. The main outcome from this analysis is that the carbonated binder does not have any significant compressive strength development after being removed from the carbonation chamber. This result can support industrial scale applications decisions highlighting that the final products would be ready to be sold and applied in construction applications right

after being removed from the carbonation chamber, thus reducing the production cycle to a few hours depending on the desired compressive strength.

2. Mineralogical and Microstructure Characterisation

As it was expected from the reactions mentioned in Chapter 2, all conditions evidenced the production of the calcium carbonates ($CaCO_3$) as the main formed product, which is responsible for the binding properties and compressive strength development. However, under optimal carbonation conditions, the binder showed a higher quantity of formed products which also explain the higher compressive strength results. The comparison of the XRD patterns before and after carbonation of the steel slag evidence the consumption of Alite (C_3S) and Belite (C_2S) and the production of calcium carbonates. It is also possible to see a few calcium silicate hydrates (CSH) carbonated during the reaction, thus producing amorphous silica gel [48]. Other researchers have found similar results through XRD [34,63,81]. On the other hand, the x-ray diffraction analysis showed some phases that did not react at all with CO_2 which were the gehlenite and wusite. Figure 9 shows x-ray diffraction analyses comparing the mineralogical phase differences between non-carbonated steel slag powder with a smashed carbonated slag binder under optimal carbonation conditions. Similar to the steel slag sample, the Portland cement had Alite and Belite as consumed phases, besides calcium carbonates and few carbonated CSH as formed products. However, it was possible to identify some ettringite and portlandite as products from the Portland cement sample since the sample also hydrated as it was mixed with water. Figure 10 shows the XRD patterns from the non-carbonated and carbonated Portland cement.

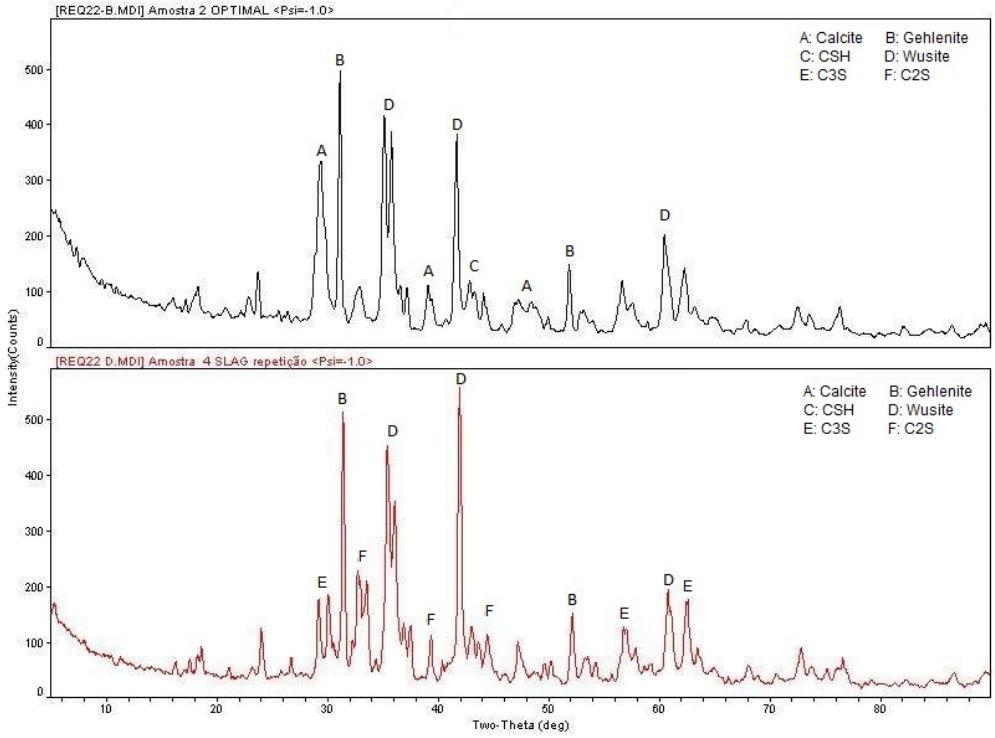

Figure 9 - XRD patterns of steel slag before (below) and after (up) carbonation.

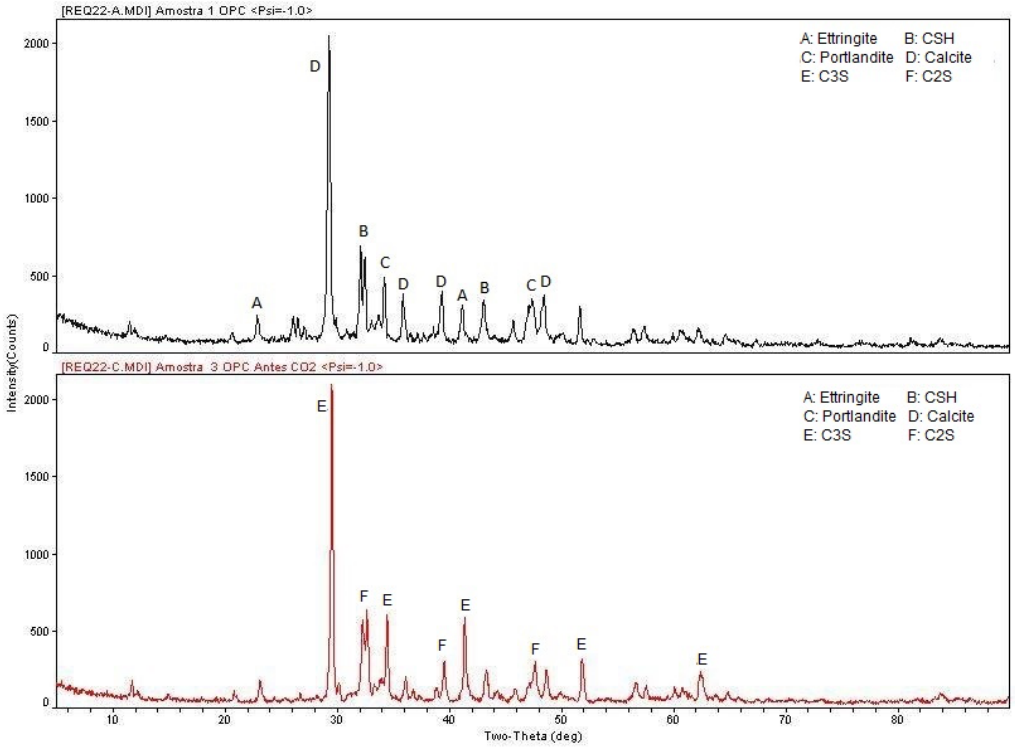

Figure 10 - XRD patterns of Portland cement before (below) and after (up) carbonation.

Through the BSE and secondary electron (SE) images, it was possible to see calcium carbonates and carbonated CSH products on the carbonated steel slag sample. Figure 11 (a) shows a BSE image of a steel slag binder section and Figure 11 (b) shows a SE image of a binder fractured sample where the products are identified together with the iron-rich non-reactive particles. Similarly, Figure 12 (a) and (b) show under a microscope scale, respectively, a BSE and a SEM image of a Portland cement carbonated binder where it is possible to see the calcium carbonates, carbonated CSH and formed ettringite.

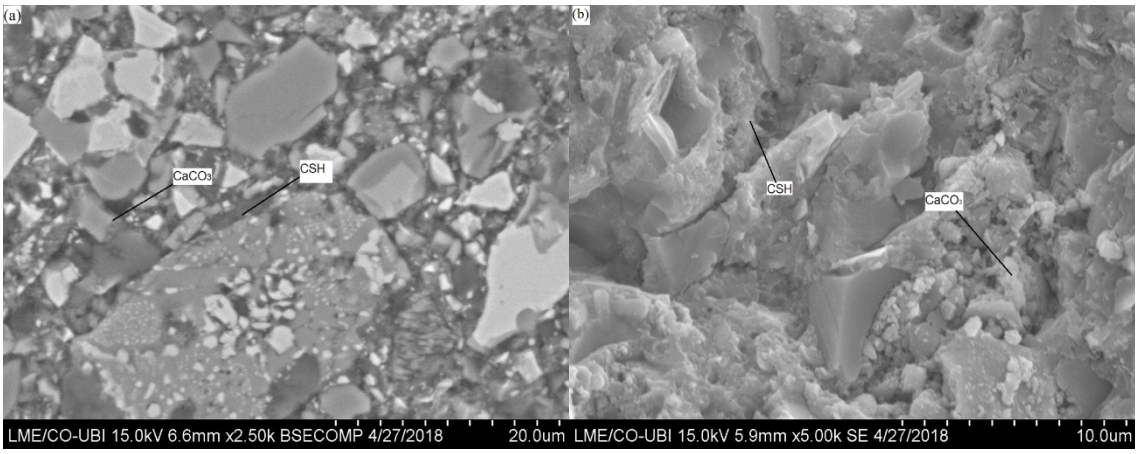

Figure 11 - Steel slag carbonated binder under a microscope scale section (a) and fracture (b).

Figure 12 - Portland cement carbonated binder under a microscope scale section (a) and fracture (b).

3. Carbonation Degree

The TG e DTG curves demonstrated that the steel slag before carbonation had only 0.48% of calcium carbonates while after carbonation this value increased to 8.83%. Due to the steel slag chemical composition, the theoretical C_{max} was 13.62% reaching a carbonation degree of 63.6%. Analyzing the TG and DTG Portland cement curves, it was possible to conclude that before carbonation the sample already had 13.81% of calcium carbonates and this value increased to 23.44% after carbonation. Due to Portland cement chemical composition, the theoretical C_{max} was 31.65 which represented the Portland cement carbonation degree as being of 54.0%. Table 12 shows the carbonation degree and calcium carbonates percentage of steel slag and Portland cement before and after carbonation. Figure 13 shows the steel slag and Portland cement TG and DTG curves.

Table 12 - Steel slag and Portland cement carbonation degree

Material	**C_0 (%)**	**C (%)**	C_{max} (%)	**Dc (%)**
Steel slag	0.48	8.83	13.62	63.6
Portland cement	13.81	23.44	31.65	54.0

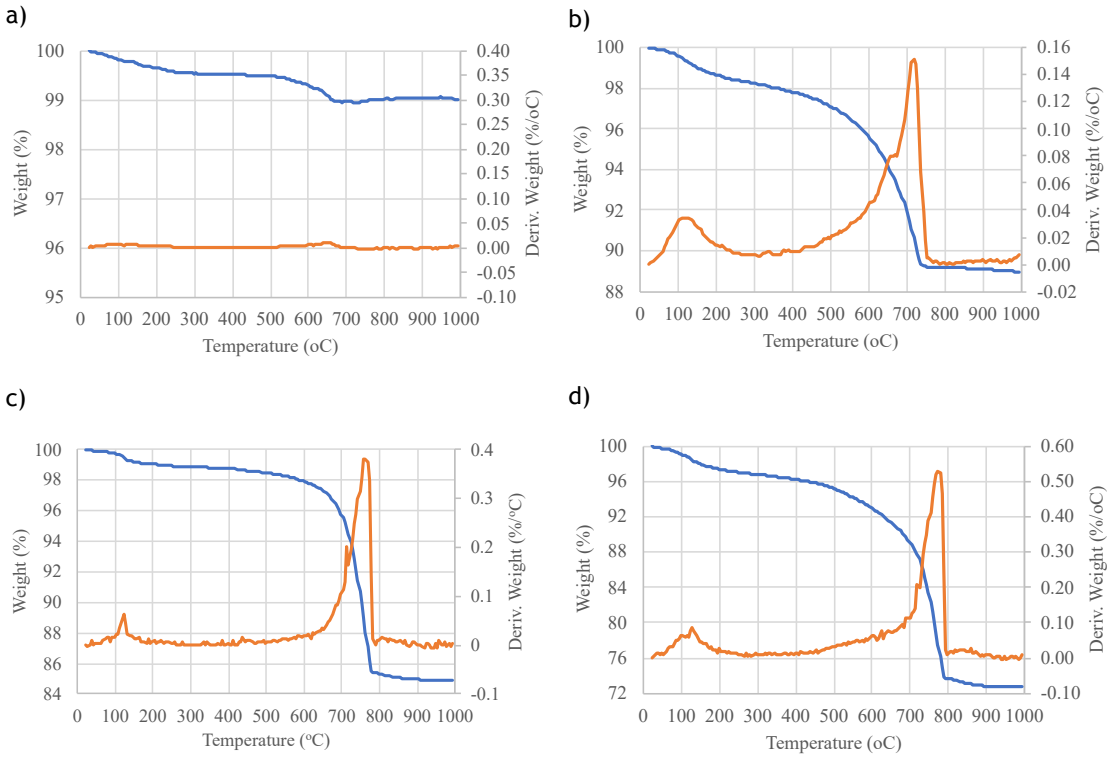

Figure 13 - Steel slag TG and DTG curves before a) and after b) carbonation and Portland cement TG and DTG curves before (c) and after (d) carbonation.

Chapter 6
Conclusion and Future Research

1. Final Considerations

The steel slag-based binder, through the compressive strength demonstrated, has great potential as Portland cement replacer for precast building applications in a wider range of applications such as masonry blocks, structural applications, and urban furniture. Moreover, the novel binder can be a game changer in the construction industry to reduce the natural resources and energy consumption to produce Portland cement and support a disruption on the construction industry towards a sustainable and carbon neutral economy. Due to its composition and wide range of applications, the steel slag-based binder can be considered as a great green alternative for proper destination and valorisation of steel slag, which is mainly dumped in landfills, donated or sold with no added value. Moreover, the binder can be considered as a permanent carbon dioxide storage, encapsulating CO_2 through the carbonation during the curing process and tackling the climate change.

2. Main Results

The thesis extensively investigated since the raw material preparation to be carbonated until the conditions that activate the binder with more efficiency. The knowledge obtained about the carbon dioxide activation for steel slag-based binders was relevant and the following conclusion can be drawn from this scientific research.

- The slag fineness is extremely relevant on the compressive strength development since the surface area is related to the powder reactivity. The finest powder reached 2.5 times higher than compressive strength on same carbonation conditions.
- The water content and the compacting pressure have a great influence on the compressive strength since the carbon dioxide diffusivity occurs with the water entering the binder matrix. However, the water content and compact pressure should be well controlled to avoid prejudice to the reaction. Optimal water content was found at 10% and compacting pressure higher than 20 MPa. Together these parameters provided a compressive strength already higher than 70 MPa.
- The temperature and carbon dioxide total pressure in the carbonation chamber has a strong influence in the reaction since less than 60ºC will not activate the steel slag well and 70ºC will reduce the reactivity as water evaporates faster. The System total pressure corroborates with the gas penetration reaching a compressive strength two times higher when compared with 3.5 and 1.5 bar.

- The steel slag binder reached excellent compressive strength results only with 24hrs of carbonation representing a potential material for the replacement of ordinary Portland cement on precast building applications. Both materials evidenced similar carbonation degree under the same conditions, thus carbonating more than 50% of its potential.
- The steel slag binder is a potential material to valorise and give sustainable meaning for the steel slag landfilled waste. By disrupting the construction industry towards an eco-friendly way, the steel slag is transformed into building construction materials as it permanently stores waste and carbon dioxide.

3. Future Research

This thesis has been oriented for the carbon activation of steel slag-based binders with the mentioned conditions and equipment. After the extensive experiments, analysing its results and understanding its potential, it is possible to suggest further research under the topic.

- Regarding the utilisation of the raw material, it would be interesting to test different calcium and magnesium-rich industrial waste in order to evaluate their efficiency and compatibility. Moreover, using wastes that are already in a powder configuration and would not require grinding would save energy, time and CO_2 emissions to the production process. It is possible to highlight lithium mining waste due to its exploitation growth based on the lithium battery demand from the global market.
- In terms of water utilisation, it would be interesting to evaluate water waste utilisation from different industries and also verify about heavy metals or toxic encapsulation.
- Regarding the carbonation conditions, it would be interesting to control the relative humidity and pH inside the chamber to understand if there is a relevant modification on the binder compressive strength development. Moreover, working with a chamber that provides its own temperature would reduce variations on carbonation duration and temperature analysis. It would be also interesting to try CO_2 rich smoke from the industry to evaluate the relationship between the carbonation duration and compressive strength development to verify if it would be feasible to use less pure CO_2 on the carbonation. Moreover, conducting the carbonation degree analysis on different conditions would give a greater comprehension about each condition effect.
- The conducted research investigated the binder formation through cylindrical samples with 2cm of diameter and 4cm of height. A size effect analysis would be important to evaluate if the carbon dioxide can penetrate in real scale building materials matrix and carbonate with similar efficiency and understand how the size would influence the compressive strength development. Moreover, it is important to evaluate the adhesion between the aggregates, binder, steel bars and further concrete properties depending on the specific application such as durability, flexural and tensile strength.

- Finally, it is also suggested to evaluate a system 100% made by steel slag-based carbon dioxide activated material where not only the binder but aggregates were also replaced by the waste and verify its feasibility for precast building applications since, this way, the environmental, circular and carbon negative potential would be increased.

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