

UNIVERSIDADE FEDERAL DE MINAS GERAIS

Programa de Pós-Graduação em Engenharia Metalúrgica, Materiais e de Minas

Tese de Doutorado

Comportamento dos elementos-traço (arsênio, cádmio, chumbo, cloro, cobre, mercúrio e níquel) no processo de sinterização piloto de minério de ferro

Autor: Lucas Ladeira Lau

Orientador: Prof. Maurício Covceovich Bagatini

Outubro/2020

UNIVERSIDADE FEDERAL DE MINAS GERAIS

Programa de Pós-Graduação em Engenharia Metalúrgica, Materiais e de Minas

Lucas Ladeira Lau

COMPORTAMENTO DOS ELEMENTOS-TRAÇO (ARSÊNIO, CÁDMIO, CHUMBO,
CLORO, COBRE, MERCÚRIO E NÍQUEL) NO PROCESSO DE SINTERIZAÇÃO DE
MINÉRIO DE FERRO.

Tese de Doutorado apresentada ao Programa de Pós-Graduação em Engenharia Metalúrgica, Materiais e de Minas da Escola de Engenharia da Universidade Federal de Minas Gerais, como requisito parcial para obtenção do Grau de Doutor em Engenharia Metalúrgica, Materiais e de Minas.

Área de Concentração: Metalurgia Extrativa.

Orientador: Prof. Maurício Covcevich Bagatini.

Belo Horizonte

Universidade Federal de Minas Gerais

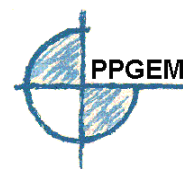
Escola de Engenharia

2020

L366c	<p>Lau, Lucas Ladeira. Comportamento dos elementos-traço (arsênio, cádmio, chumbo, cloro, cobre, mercúrio e níquel) no processo de sinterização de minério de ferro [recurso eletrônico] / Lucas Ladeira Lau. - 2020. 1 recurso online (xiii, 82 f. : il., color.) : pdf.</p> <p>Orientador: Maurício Covcevic Bagatini.</p> <p>Tese (doutorado) - Universidade Federal de Minas Gerais, Escola de Engenharia.</p> <p>Anexos e apêndices: f. 73-82.</p> <p>Inclui bibliografia. Exigências do sistema: Adobe Acrobat Reader.</p> <p>1. Engenharia metalúrgica - Teses. 2. Metalurgia extrativa - Teses. 3. Ar - Poluição - Teses. 4. Elementos traços - Teses. 5. Metais pesados - Teses. 6. Sinterização - Teses. I. Bagatini, Maurício Covcevic. II. Universidade Federal de Minas Gerais. Escola de Engenharia. III. Título.</p>
	CDU: 669(043)



UNIVERSIDADE FEDERAL DE MINAS GERAIS
ESCOLA DE ENGENHARIA
Programa de Pós-Graduação em Engenharia
Metalúrgica, Materiais e de Minas



Tese intitulada "**Comportamento dos Elementos-traço (Arsênio, Cádmiu, Chumbo, Cloro, Cobre, Mercúrio e Níquel) no Processo de Sinterização de Minério de Ferro**", área de concentração: Metalurgia Extrativa, apresentada pelo candidato **Lucas Ladeira Lau**, para obtenção do grau de Doutor em Engenharia Metalúrgica, Materiais e de Minas, aprovada pela comissão examinadora constituída pelos seguintes membros:

Prof. Maurício Covceвич Bagatini
Orientador - Dr. (UFMG)

Prof. Leandro Rocha Lemos
Dr. (UFMG)

Flávio de Castro Dutra
Dr. (VALE S/A)

Profª Júnia Soares Alexandrino
Drª (UEMG)

Maycon Athayde
Dr. (VALE S/A)

Prof. Rodrigo Lambert Oréfice
Coordenador do Programa de Pós-Graduação em Engenharia
Metalúrgica, Materiais e de Minas/UFMG

Belo Horizonte, 29 de outubro de 2020

Dedico este trabalho a toda a minha família pelo incansável apoio durante toda a minha trajetória acadêmica e profissional.

Agradecimentos

O autor agradece a todos aqueles que, direta ou indiretamente, colaboraram na preparação deste trabalho e, em particular:

Ao Prof. Luiz Fernando Andrade de Castro pelo apoio, dedicação, amizade e pela oportunidade que me permitiu grande crescimento acadêmico, ao Prof. Maurício Covcevich Bagatini, pela atenção e disposição para contribuir com o trabalho, mesmo recebendo a orientação em momento tardio do doutorado, e à Prof. Aline Lima da Silva, que recebeu o trabalho também em momento tardio e se mostrou sempre disposta a ajudar.

À Vale, por todo o apoio técnico durante o trabalho. Em especial aos amigos engenheiros Valdirene Resende, Alei Domingues e Flávio de Castro Dutra, que contribuíram de forma direta para o desenvolvimento técnico deste trabalho.

À todos os demais técnicos e funcionários do CTF – Centro de Tecnologia de Ferrosos da Vale, que contribuíram de forma direta, ou indireta, na execução dos inúmeros testes realizados.

À minha esposa, Thiara, por compreender a necessidade de dedicação ao trabalho e por não me deixar desanimar, me incentivando a buscar cada vez mais e a fazer sempre o meu melhor.

À minha família e amigos, por acreditarem em mim e me apoiarem nas difíceis decisões que tomei e me possibilitaram realizar este estudo.

SUMÁRIO

LISTA DE FIGURAS.....	viii
LISTA DE TABELAS.....	ix
LISTA DE NOTAÇÕES.....	x
RESUMO.....	xii
ABSTRACT.....	xiii
Capítulo 1. Introdução, Objetivos e Estrutura da Tese.....	1
1.1 Introdução.....	1
1.2 Objetivos.....	4
1.3 Estrutura da Tese.....	5
1.4 Referências.....	6
Capítulo 2. Artigo A – Trace elements emission in sintering: A Review.....	7
2.1 Introduction.....	8
2.2 Emissions of trace elements in high-temperature industrial processes.....	9
2.2.1 Coal-fired power station.....	10
2.2.2 Combustion processes of sewage sludge.....	12
2.2.3 Ironmaking and Steelmaking.....	14
2.3 Iron ore sintering.....	16
2.3.1 Iron ore sintering air pollutants.....	18
2.3.2 Source of trace elements in the iron ore sintering process.....	19
2.3.3 The behavior of trace elements.....	19
2.3.4 Trace elements emissions factors.....	24
2.3.5 Measurements used in studies/industry.....	24
2.3.6 Air Pollution Control Devices (APCD) employed / available.....	26
Electrostatic Precipitator (ESP).....	26
Fabric filter (FF).....	27
Cyclones.....	27
Wet Fine Scrubber.....	28

Flue Gas Desulfurization (FGD).....	28
Selective Catalytic Reduction	29
APCDs configurations and efficiency in retaining trace elements.....	29
2.4 Conclusions.....	32
2.5 Acknowledgments	32
2.6 References.....	32
Capítulo 3. Artículo B - Evaluation of Trace Elements Behavior in Iron Ore Sintering Process.....	43
Abstract.....	43
3.1 Introduction	44
3.2 Materials and Methods	45
3.2.1 Raw Materials	45
3.2.2 Sintering tests	46
3.2.3 Trace elements evaluation	47
3.3 Results and discussion.....	49
3.3.1 Sintering conditions.....	49
3.3.2 Trace elements in the mixture	49
3.3.3 Trace elements in the sinter	51
3.3.4 Trace elements distribution	51
Arsenic	55
Cadmium	56
Copper.....	56
Nickel.....	57
Mercury	58
Lead	59
Chlorine	60
3.3.5 Analysis of atmospheric emissions.....	61
3.4 Conclusions.....	63

3.5 Acknowledgment.....	63
3.6 References.....	64
Capítulo 4. Considerações finais.....	68
4.1 Conclusões gerais.....	68
4.2 Contribuições originais ao conhecimento	71
4.3 Sugestões para trabalhos futuros.....	72
APÊNDICE A – Resultados do balanço de massa	73
APÊNDICE B – Resultados da análise de gás.....	74
ANEXO A – Characterization and mass balance of trace elements in an iron ore sinter plant.....	75

LISTA DE FIGURAS

Figure 2.1 - Schematic diagram showing the material flow in a sinter plant (adapted from Wielgosinski and Łechtańska [58].	17
Figure 2.2 - Temperature profile and the atmosphere regime of the sintering bed (adapted from Cores <i>et al.</i> [57])......	17
Figure 2.3 - Paths that trace elements can follow in iron ore sintering process (adapted from Xu <i>et al.</i> [6])......	21
Figure 2.4 - Classification of trace elements based on their volatilization [6, 30, 69, 70].	22
Figure 3.1 - Schematic representation of the pilot sintering used in the tests.....	47
Figure 3.2 – Temperature profile of the sinter pot test.	49
Figure 3.3 - Recovery and emission factors for total trace elements in each mixture...53	53
Figure 3.4 - Recovery and emission factors for arsenic in each mixture.	55
Figure 3.5 - Recovery and emission factors for cadmium in each mixture.	56
Figure 3.6 - Recovery and emission factors for copper in each mixture.....	57
Figure 3.7 - Recovery and emission factors for nickel in each mixture.....	58
Figure 3.8 - Recovery and emission factors for mercury in each mixture.....	59
Figure 3.9 - Recovery and emission factors for lead in each mixture.....	60
Figure 3.10 - Recovery and emission factors for Chlorine in each mixture.	61
Figure 3.11 - Trace element concentration in atmospheric emission.	62

LISTA DE TABELAS

Table 2.1 - Summary of the concentrations of TEs in diverse coal samples [29, 33-35].	10
Table 2.2 – Summary of the concentrations of TEs in diverse sewage sludge samples in g/t of dry solid sewage sludge [3, 40, 42, 43].....	12
Table 2.3 – Elemental composition in mg/g of particulates emitted by the stages of the steelmaking process [48, 49].....	15
Table 2.4 – Trace element composition of iron ore sintering raw materials in ppm [22, 50, 53, 65-67].	20
Table 2.5 - Trace elements emission factor in iron ore sintering (mg/t sinter) [26, 81].	25
Table 2.6 - Trace element control efficiencies in different APCD technologies in % of retention [93].	30
Table 2.7 - Trace elements removal efficiency of 7 different APCD combinations in coal- fired power plants in China [34].	31
Table 3.1 - Composition of sintering mixtures used in the tests (in mass percentage).	46
Table 3.2 – Sintering conditions.	49
Table 3.3 - Chemical characterization of the mixtures used in the tests.....	50
Table 3.4 - Chemical analysis of sinter.	52
Table 3.5 - Amount of trace elements classified as non-volatile, semi-volatile, and volatile in the mixtures.....	53
Table 3.6 - Spearman’s Correlation between emission factor and chemical composition of mixture.	54

LISTA DE NOTAÇÕES

AAS: Atomic Absorption Spectrometry

ACI: Activated Carbon Injection

BIF: Bromide Injection into the Furnace

AFGD: Ammonia Flue Gas Desulphurization

APCD: Air Pollution Control Device

BF: Blast Furnace

BOF: Basic Oxygen Furnace

CFB-FGD: Circulating Fluidized-Bed Flue Gas Desulphurization

CBz: Chlorobenzene

C_m : Trace element concentration in sinter mixture

C_s : Trace element concentration in sinter

DFA-FGD: Dense Flow Absorber Flue Gas Desulphurization

EFF: Electric fabric Filter

EPA: Environmental Protection Agency

ESCS: Electrostatic Space Cleaner Super

ESP: Electrostatic Precipitator

FF: Fabric Filter

FGD: Flue Gas Desulfurization

Hg_P : Particle-bound mercury

ICP-AES: Inductively Coupled Plasma - Atomic Emission Spectroscopy

ICP-MS: Inductively Coupled Plasma - Mass Spectrometry

LLT-ESP: Low-Temperature Electrostatic Precipitators

MEEP: Moving Electrode Electrostatic Precipitator

NO_x: Nitrogen Oxides

OMS: Organização Mundial da Saúde

PAH: Polycyclic Aromatic Hydrocarbon

PBDD/F: Polybrominated Dibenzo-P-Dioxins/Dibenzofuran

PBDE: Polybrominated Diphenyl Ether

PCB: Polychlorinated Biphenyls

PCDD/F: Polychlorinated Dibenzo-P-Dioxins/Dibenzofurans

PCN: Polychlorinated Naphthalene

PM: Particulate Matter

PM_{2.5}: Particulate Matter smaller than 2.5 micrometers

PM₁₀: Particulate Matter smaller than 10 micrometers

pO₂: Partial Oxygen Pressure

p-value: Significance level

r-value: Pearson Correlation Coefficient

SCR: Selective Catalytic Reduction

SMC: Special Mercury Control Technology

SNCR: Selective Non-Catalytic Reduction

SO_x: Sulfur Oxide

TE: Trace element

WESP: Wet Electrostatic Precipitators

WFGD: Wet Flue Gas Desulphurization

WHO: World Health Organization

x_E: Emission factor

x_R: Recovery factor

ρ: Spearman's Correlation coefficient

RESUMO

As questões relacionadas aos impactos ambientais provocados pela indústria têm se tornado mais relevante a cada dia, levando a maiores restrições nas legislações ambientais. A indústria siderúrgica, notadamente conhecida pela sua elevada geração de poluentes atmosféricos, deposita especial atenção no controle desse tipo de emissão. Dentre as emissões que têm obtido atenção nas legislações modernas estão os elementos-traço, devido ao relevante impacto causado por tais poluentes ao meio ambiente e à saúde humana. Neste cenário, a presente tese avaliou o comportamento dos elementos-traço no processo de sinterização piloto de minério de ferro através de balanço de massa e análise de gás, realizados em ensaio em planta piloto de sinterização, embasando e contextualizando os resultados com o conhecimento disponível na literatura. Observou-se três comportamentos distintos entre os elementos-traço. Alguns elementos permanecem majoritariamente no estado sólido durante o processo, como é o caso do cobre e do níquel. Outros elementos-traço volatilizam parcialmente e recondensam ao longo do sistema de exaustão dos gases, como o cádmio, o chumbo e o arsênio. Já o mercúrio e o cloro volatilizam e são emitidos ainda na forma gasosa. No presente estudo identificou-se que os principais fatores que afetam a emissão dos elementos-traço são as características físicas e químicas dos insumos, as condições do processo e os mecanismos de controle de emissão adotados. Embora nem sempre seja possível, a escolha de insumos com baixa concentração de elementos-traço tem impacto direto nas emissões. Insumos com menor teor de cloro possuem impacto positivo na redução das emissões de alguns elementos-traço, como cobre, níquel e arsênio, devido à formação de cloretos. Do ponto de vista do processo, ainda que diversos outros parâmetros precisem ser considerados, uma menor temperatura de queima, uma atmosfera menos oxidante e menor presença de cloretos e sulfetos reduzem a volatilização e, conseqüentemente, a emissão dos elementos-traço. Por fim, a escolha adequada das tecnologias de abatimento das emissões possui forte impacto na emissão destes elementos. Por meio de uma revisão bibliográfica extensa identificou-se que embora tecnologias específicas para controle de elementos-traço não sejam usuais, a maior parte dos elementos podem ser retidos em equipamentos com alta eficiência no controle das emissões de materiais particulados finos. Os elementos com maior tendência a serem emitidos na forma gasosa são mais difíceis de serem retidos com as tecnologias convencionais, sendo necessários o uso de técnicas alternativas, como o uso de adsorventes para a captura destes elementos.

ABSTRACT

The issues related to the environmental impacts caused by the industry have become more relevant every day, leading to greater restrictions in environmental legislation. The steel industry, notably known for its high generation of air pollutants, pays special attention to the control of this type of emission. Trace elements are among the pollutants that have received attention in modern legislation, due to the relevant impact caused by such pollutants on the environment and human health. In this scenario, this thesis evaluated the behavior of the trace elements in a pilot iron ore sintering process through mass balance and gas analysis, carried out in a test at a pilot sintering plant, basing and contextualizing the results with the knowledge available in literature. Three distinct behaviors were observed between the trace elements. Some elements remain mostly in the solid state during the process, such as copper and nickel. Other trace elements partially volatilize and recondense along the exhaust gas system, such as cadmium, lead and arsenic. Mercury and chlorine volatilize and are emitted in gaseous form. In the present study, it was identified that the main factors that affect the behavior of the trace elements are the physical and chemical characteristics of the inputs, the process conditions and the emission control mechanisms adopted. Although it is not always possible, the choice of raw materials with a low concentration of trace elements has a direct impact on emissions. It has also been shown that raw materials with less chlorine content have a positive impact on reducing emissions of some trace elements, such as copper, nickel and arsenic. From the process, in general, a lower burning temperature, a less oxidizing atmosphere and less presence of chlorides and sulfides reduce volatilization and, consequently, the emission of trace elements. Finally, the appropriate choice of air pollution control devices has a strong impact on the emission of these elements. Through an extensive bibliographic review it was identified that although specific technologies for the control of trace elements are not usual, most elements can be retained in equipment with high efficiency in controlling the emissions of fine particulate materials. The elements most likely to be emitted in gaseous form are more difficult to be retained with conventional technologies, requiring the use of alternative techniques, such as the use of adsorbents to capture these elements.

Capítulo 1. Introdução, Objetivos e Estrutura da Tese

1.1 Introdução

A siderurgia é considerada uma das principais atividades industriais do mundo, uma vez que praticamente qualquer produto utilizado na sociedade moderna ou possui algum componente de aço ou necessitou de aço durante seu processo de fabricação. De acordo com a OMS (Organização Mundial da Saúde) a siderurgia é responsável por significativa poluição atmosférica, principalmente em países em desenvolvimento (ZHOU; STREZOV; JIANG; YANG *et al.*, 2020). Entre as emissões, o material particulado emitido pela indústria siderúrgica apresenta extensa variedade de elementos-traço.

Elementos-traço são elementos químicos encontrados em concentrações muito baixas, usualmente da ordem de miligramas por quilogramas (mg/kg) ou partes por milhão (ppm). Muitos deles são considerados poluentes atmosféricos perigosos e são classificados como metais pesados, sendo caracterizados como o grupo de metais e metaloides com densidade atômica superior a 4 g/cm^3 (NALBANDIAN, 2012; ZHU; TIAN; CHENG; LIU *et al.*, 2016).

As atividades industriais, de maneira geral, impactam diretamente na concentração de elementos-traço na atmosfera, podendo causar severos impactos aos ecossistemas e à saúde humana, através da contaminação do solo e da água. Estes elementos possuem longos tempos de residência e são facilmente assimilados pelos organismos, podendo ser absorvidos pelas plantas e entrar na cadeia alimentar em quantidades significativas. Portanto, o consumo de frutas e vegetais cultivados em solos com elevadas concentrações de elementos potencialmente tóxicos representa uma preocupação no contexto da saúde pública.

Elementos-traço podem se acumular no tecido adiposo e no sistema circulatório, afetando o sistema digestivo, o sistema cardiovascular e o sistema nervoso central. Ou seja, eles podem ser agravantes para outras doenças, sendo alguns deles, inclusive, considerados carcinogênicos para humanos. Recentemente foram relatados diversos incidentes envolvendo contaminação por metais pesados, especialmente na China, onde mais de 30 casos de envenenamento por metais pesados foram registrados entre 2009 e 2016 (SI; XIN; ZHANG; LI *et al.*, 2019; TIAN; LIU; ZHOU; LU *et al.*, 2014; ZHAO; DUAN; TAN; LIU *et al.*, 2016; ZHU; TIAN; CHENG; LIU *et al.*, 2016).

No contexto da indústria siderúrgica, a maior parte da produção mundial de aço é realizada através do processo com alto-forno e convertedor BOF (Basic Oxygen Furnace). Para a carga ferrosa dos altos-fornos são necessárias algumas características, que podem ser obtidas no minério granulado ou através de processos de aglomeração de finos de minério. O principal processo de aglomeração utilizado pela siderurgia mundial é a sinterização, sendo o sinter responsável pela maior parte da carga ferrosa dos altos-fornos. Nesse processo uma mistura composta por finos de minério, fundentes, resíduos da siderurgia e combustível passam por um processo de aglomeração a altas temperaturas, a fim de se obter as características físico-químicas e mecânicas adequadas ao alto-forno.

Em processos de alta temperatura, como a sinterização, os elementos-traço podem volatilizar, condensar, adsorver e se transformar quimicamente, potencialmente resultando na sua emissão na forma gasosa ou como material particulado, concentrando-se, principalmente, nas partículas mais finas. O comportamento de cada elemento-traço durante o processo de alta temperatura tem relação com as suas características de volatilização, que depende da sua forma de ocorrência, das suas propriedades, concentração e das condições de processo, como a temperatura de combustão, atmosfera e outros.

A produção de ferro gusa no alto-forno apresenta o maior impacto na emissão de gases de efeito estufa entre os processos de uma usina siderúrgica integrada, entretanto a sinterização é o processo que mais contribui para as emissões de material particulado e de gases e é o maior responsável pela emissão de metais (BURCHART-KOROL, 2013). Embora exista uma extensa variedade de tecnologias para controle de emissões de poluentes atmosféricos, podendo ser utilizadas em diversas combinações, no geral elas não foram desenvolvidas para o controle da emissão de elementos-traço, sendo este um objetivo “secundário” do processo. Desta forma, a eficiência desses equipamentos no controle das emissões de elementos-traço varia bastante e seu efeito está, normalmente, relacionada ao abatimento da emissão de materiais particulados.

A literatura apresenta uma série de estudos voltados para emissões atmosféricas de elementos-traço, porém a emissão desses elementos na siderurgia, em especial na sinterização, ainda é pouco explorada. As emissões de elementos-traço nos processos de produção de energia em termelétricas a carvão e a pirólise de resíduos sólidos urbanos foi bastante estudada. Esses estudos trabalharam principalmente com balanços de massa, visando entender a eficiência dos diversos métodos de controle das

emissões atmosféricas e o impacto da adoção de matérias-primas alternativas nos processos de geração de energia. Do ponto de vista da sinterização, a maior parte dos poucos estudos disponíveis, está relacionada à emissão de materiais particulados, os quais podem possuir concentrações significativas de elementos-traço.

Para enfrentar os impactos ambientais e à saúde causados pelos elementos-traço, as legislações ambientais têm se tornado mais restritivas para as emissões destes elementos e dos materiais particulados nos quais eles se encontram. A União Europeia, por exemplo, possui restrição para a concentração de $PM_{2,5}$ (material particulado com diâmetro menor do que 2,5 micrômetros), chumbo, arsênio, cádmio e níquel no ar. Já nos Estados Unidos, Brasil e China, são determinados limites de concentração no ar para $PM_{2,5}$ e chumbo.

Diante do contexto apresentado, a compreensão dos aspectos envolvidos na emissão dos elementos-traço no processo de sinterização de minério de ferro torna-se cada vez mais urgente. Neste sentido, este trabalho busca contribuir para a compreensão do comportamento dos elementos-traço no processo de sinterização de minério de ferro. Para tal foram escolhidos sete elementos-traço em função da existência de legislação ambiental restringindo sua emissão, da concentração desses elementos nas matérias-primas da sinterização, em especial o sinter feed, da participação desses elementos nos processos de formação de outros poluentes e na teórica presença deles nas emissões atmosféricas. Os elementos escolhidos foram o arsênio, o cádmio, o chumbo, o cloro, o cobre, o mercúrio e o níquel, que foram estudados através de experimentos em planta piloto e revisão bibliográfica expandida, a qual engloba dados consolidados de outros processos industriais de alta temperatura.

1.2 Objetivos

O objetivo geral do presente trabalho é compreender o comportamento dos elementos arsênio, cádmio, chumbo, cloro, cobre, mercúrio e níquel no processo de sinterização de minério de ferro. De acordo com o objetivo geral, os seguintes objetivos específicos foram traçados para o desenvolvimento do presente trabalho:

- Realizar revisão bibliográfica expandida e análise crítica de processos de alta temperatura com base de dados consistente no que tange o comportamento de elementos-traço e dispositivos de controle das suas emissões;
- Avaliar o aporte de elementos-traço na sinterização de minério de ferro através da caracterização química das matérias-primas e insumos empregados na sinterização;
- Determinar a partição de elementos-traço através de experimentos em escala piloto e balanço de massa;
- Identificar o comportamento de cada um dos elementos-traço avaliados e apresentar alternativas de sistemas para abatimento dos mesmos disponíveis na indústria, baseado em revisão bibliográfica.

1.3 Estrutura da Tese

A presente tese foi redigida a partir de dois artigos submetidos para publicação em periódicos internacionais. A tese se divide em quatro capítulos, sendo o primeiro composto pela introdução, objetivos e estrutura da tese, que visa esclarecer a importância do tema e as lacunas de conhecimento, o propósito do estudo e a estrutura do documento.

O Capítulo 2 corresponde ao artigo "*Trace elements emission in sintering: A Review*", submetido para publicação em periódico classificado no Qualis Capes (quadriênio 2013-2016) como A1. Nesse estudo foi coletado e consolidado o conhecimento disponível acerca da emissão de elementos-traço na sinterização de minério de ferro, complementando com trabalhos correlatos de outros processos industriais de alta temperatura. Ainda foram discutidos os dispositivos de controle de emissões atmosféricas e sua eficiência no combate às emissões de elementos-traço. De tal forma foi possível construir uma visão crítica voltada para o comportamento desses elementos no processo de sinterização de minério de ferro.

O Capítulo 3 corresponde ao artigo "*Evaluation of Trace Elements Behavior in Iron Ore Sintering Process*", submetido para publicação em periódico classificado no Qualis Capes (quadriênio 2013-2016) como A2. Esse estudo teve como objetivo entender as partições e o comportamento de sete elementos-traço (arsênio, cádmio, chumbo, cloro, cobre, mercúrio e níquel) durante o processo de sinterização em planta piloto. Para tal foram realizados experimentos com seis diferentes misturas de sinterização e o balanço de massa dos elementos-traço para cada uma das misturas. Além disso, para três dessas misturas foi efetuada análise do gás de emissão e os resultados obtidos comparados aos do balanço de massa.

Já o Capítulo 4 refere-se às considerações finais, onde os resultados obtidos no Capítulo 3 são confrontados com os dados da literatura apresentados no Capítulo 2. Os resultados mais relevantes são discutidos e as lacunas ainda existentes no conhecimento concernente a esse tema são apontadas. Ainda no Capítulo 4 são apresentadas as contribuições originais para o conhecimento e as sugestões para trabalhos futuros. Tais considerações se justificam, uma vez que ainda existe um longo caminho para a efetiva compreensão dos diversos mecanismos envolvidos na formação e emissão de elementos-traço no processo de sinterização de minério de ferro.

Os apêndices A e B apresentam, respectivamente, os resultados detalhados obtidos no balanço de massa e na análise de gás efetuados na planta piloto. Por fim, o anexo A apresenta um artigo publicado previamente ao período de doutorado, no periódico *Journal of Materials Research and Technology*. Nesse trabalho diversos tipos de minério e insumos da sinterização de minério de ferro foram caracterizados quimicamente quanto a presença de elementos-traço e os resultados desse trabalho são utilizados na discussão do Capítulo 4.

1.4 Referências

BURCHART-KOROL, D. Life cycle assessment of steel production in Poland: a case study. **Journal of Cleaner Production**, 54, p. 235-243, 2013/09/01/ 2013.

NALBANDIAN, H. **Trace element emissions from coal**. IEA Clean Coal Centre. 2012. (ISBN 978-92-9029-523-5).

SI, R.; XIN, J.; ZHANG, W.; LI, S. *et al.* Source apportionment and health risk assessment of trace elements in the heavy industry areas of Tangshan, China. **Air Quality, Atmosphere & Health**, 12, n. 11, p. 1303-1315, 2019/11/01 2019.

TIAN, H.; LIU, K.; ZHOU, J.; LU, L. *et al.* Atmospheric Emission Inventory of Hazardous Trace Elements from China's Coal-Fired Power Plants—Temporal Trends and Spatial Variation Characteristics. **Environmental Science & Technology**, 48, n. 6, p. 3575-3582, 2014/03/18 2014.

ZHAO, S.; DUAN, Y.; TAN, H.; LIU, M. *et al.* Migration and Emission Characteristics of Trace Elements in a 660 MW Coal-Fired Power Plant of China. **Energy & Fuels**, 30, n. 7, p. 5937-5944, 2016/07/21 2016.

ZHOU, X.; STREZOV, V.; JIANG, Y.; YANG, X. *et al.* Contamination identification, source apportionment and health risk assessment of trace elements at different fractions of atmospheric particles at iron and steelmaking areas in China. **PLOS ONE**, 15, n. 4, p. e0230983, 2020.

ZHU, C.; TIAN, H.; CHENG, K.; LIU, K. *et al.* Potentials of whole process control of heavy metals emissions from coal-fired power plants in China. **Journal of Cleaner Production**, 114, p. 343-351, 2016/02/15/ 2016.

Capítulo 2. Artigo A – Trace elements emission in sintering: A Review

Lucas Ladeira Lau^{a*}, Vladimir Strezov^b, Maurício Covcevich Bagatini^a

^a*Programa de Pós-Graduação em Engenharia Metalúrgica, Materiais e de Minas, Universidade Federal de Minas Gerais, 6627 Antônio Carlos Avenue, Engineering School, Block 2, Room 2230, Belo Horizonte, MG, Brazil, 31270-901*

^b*Department of Earth and Environmental Sciences, Faculty of Science and Engineering, Macquarie University NSW 2109, Australia*

*Corresponding author.

Iron ore sintering is one of the main activities responsible for particulate matter and trace element emissions of integrated steel plants. Due to the high environmental and human health impacts caused by trace elements, legislations are becoming more stringent for regulating emissions of the trace elements. This review consolidates several studies in the sector, focusing on the sources, behavior, and technologies employed to control emissions of trace elements during iron ore sintering. The emission of trace elements is strongly dependent on the characteristics of raw materials, operating parameters and technologies used for their abatement. Iron ore is the main responsible material for emissions of trace elements during sintering as it undergoes a series of physicochemical transformations throughout the process. In general, trace elements may remain in the solid-state, volatilize during combustion and recondense in the cleaning system, or remaining in the gaseous state during the flue gas treatment. Although most trace elements are retained in air pollution control devices in the form of particulates, volatile and semi-volatile elements (As, Se, Hg, Cd, etc) can remain as gases or concentrate in the finer particulates. Modern technologies have demonstrated high efficiency in removing these elements from the flue gases.

Keywords: air pollution control devices; atmospheric emissions; heavy metals

2.1 Introduction

Trace elements (TEs) are chemical elements found in very low concentrations, usually in the order of milligrams per kilogram (mg/kg) or parts per million (ppm) [1]. Although some elements are essential for human health and ecosystems, they are all considered to be toxic at some threshold concentration, including some being considered carcinogenic to humans (As, Cd, Cr (VI), Ni) [2-4].

TEs can behave in different ways when submitted to high-temperature processes. Some of them tend to remain in the solid-state (V, Cr, Mn, Co, Ni), others partially volatilize, and may recondense again before being emitted to the atmosphere (Zn, Pb, Cd, As), and some volatilize remaining in vapor phase until emitted to the atmosphere (Hg, F, Cl, Br) [5, 6]. The elements that volatilize can be emitted in the form of gas or fine particles, especially particulate matter smaller than 10 micrometers (PM_{10}) and smaller than 2.5 micrometers ($PM_{2.5}$), being able to travel great distances in the atmosphere before depositing, contaminating the soil and water, and entering the food chain through vegetables and fish [7-10]. Some elements are chemically stable and tend to accumulate in human tissues and the environment [3].

With increasing concerns for environmental preservation and control of the factors that impact human health, environmental legislations have also become increasingly strict. As a result, some regulations established limits to the emissions of some pollutants that were not previously controlled, such as TEs and fine particles. European legislation, for example, has limits for the concentration of $PM_{2.5}$, lead, arsenic, cadmium and nickel in the air [11]. In the United States, the Environmental Protection Agency (EPA) has air quality concentration standards for $PM_{2.5}$ and lead [12, 13]. Following other countries and the World Health Organization (WHO), in 2018 Brazil also defined its concentration limits in the air for $PM_{2.5}$ and lead [14]. The same occurred in China by set its current limits for $PM_{2.5}$ and lead in 2012 [15].

In 2005 WHO defined air quality guidelines for four pollutants, including PM_{10} and $PM_{2.5}$ [16]. In 2015 WHO selected 32 pollutants, classifying them into 4 groups according to the need for a systematic review of standards. Among TE-related pollutants, PM was classified in group 1, cadmium, chromium and lead in group 2, arsenic, manganese, platinum and vanadium in group 3, and mercury in group 4, with group 1 being the highest priority while group 4 lowest priority [17].

Iron and steel production is considered to be one of the main industries in the world, generating an approximate value of \$ 900 Bi per year, and practically all products used in the modern world either have some element of steel or need steel during their production process [18]. World steel production reached 1,869.9 Mt in 2019 [19], where around 70% of global production relies directly on inputs of coal via the BF/BOF (Blast Furnace and Basic Oxygen Furnace) route. China represents more than half of world production and it is mainly based with around 90% on the BF/BOF processes [20]. (WSA)

Sintering and pelletizing are iron ore agglomeration processes that allow the use of ores with a size lower than 10 mm in the blast furnace, without impairing the furnace's permeability [20]. Sintering is the most widely used agglomeration process in the world for ferrous burden preparation to the blast furnace, as sinter is cheaper than pellet and has better reducibility characteristics than lump. Typically, the sinter corresponds to more than 60% of the ferrous load of blast furnaces in eastern Asia [21].

Since the production of iron and steel is carried out at high temperatures and with a large quantity and variety of raw materials, this industry has a high polluting potential. Among all the processes involved in the production of steel, sintering is the main emitter of polluting gases and particles that contain TEs, being responsible for approximately 45% of the total emissions of an integrated steel plant [22-27]. The entire context presented, given the continuous growth in steel production in the world [19], strongly justifies the study of emissions of TEs in the iron ore sintering process. Given the scarcity of specific research in the area, this work collects and consolidates the still insipient knowledge on the subject, complementing it with works on TEs in other high-temperature industrial processes, such as coal-fired power plants and combustion of sewage sludge.

2.2 Emissions of trace elements in high-temperature industrial processes

Although there are not many studies on the emission of trace elements in the iron ore sintering process, works regarding these emissions in other high-temperature processes are more common. Understanding the TEs behavior in other contexts can greatly assist to elucidate their behavior in the iron ore sintering, especially when they have common raw materials or process conditions.

2.2.1 Coal-fired power station

Coal-fired power plants are responsible for almost 40% of all electrical energy generated in the world and are considered as one of the main anthropogenic sources of TE emissions, in addition to SO₂, NO_x and PM [28, 29]. A report published by the Environmental Protection Agency (EPA) points to the mercury emitted by coal-fired power plants as the hazardous air pollutant with the greatest potential to damage public health [8]. Thus, several studies address the emissions of TEs in this process.

Similar to iron ore sintering, emissions of TEs in coal-fired power stations depend on the concentration of the element in the inputs (in this case coal), the chemical and physical properties of the element, process conditions and parameters (especially firing temperature and atmosphere) and the emission control equipments used [18, 30-32].

Several authors have characterized diverse samples of coal from different regions of the world. Table 2.1 presents a summary of the concentrations of TEs identified by some authors [29, 33-35].

Table 2.1 - Summary of the concentrations of TEs in diverse coal samples [29, 33-35].

	Average (ppm)	Min (ppm)	Max (ppm)	Number of samples
Cr	33.645	6.7	394.0	26
Mn	148.1	116.2	180.0	2
Co	6.0	5.1	7.0	3
Ni	12.92	5.78	22.15	21
Cu	14.87	11.1	17.5	3
Zn	31.33	23.0	38.0	3
As	4.99	0.37	13.45	41
Mo	2.5	2.2	2.7	3
Ag	0.006	0.006	0.006	1
Cd	0.424	0.008	1.12	26
Sb	1.253	0.50	3.24	21
Ba	184.67	150.0	245.0	3
Pb	20.54	7.8	30.6	26
Hg	0.141	0.02	0.35	38
Se	2.88	0.87	5.43	38

The main form that mercury is found in coal is linked to organic matter or sulfides. There are three ways in which Hg can be emitted from coal-fired power plants, elemental mercury (Hg⁰), gaseous oxidized mercury (Hg²⁺), and particle-bound mercury (Hg_P) [10, 32]. During firing in the furnace, mercury is emitted in its elemental form (Hg⁰). As the

temperature of the gas reduces, mercury can react with several elements, such as O_2 , HCl , Cl_2 , SO_2 , NO , NO_2 , N_2O , NH_3 or H_2S , forming oxidized mercury (HgO , Hg_2Cl_2 , $HgCl_2$). Oxides of transition metals, such as CuO and Fe_2O_3 , as well as carbon, can also cause oxidation of mercury. This process results in formation of particulate mercury [33, 36]. According to Zheng *et al.* (2018), presence of Cl in coal results in the formation of $HgCl_{2(g)}$, resulting in the adsorption of Hg in fly ashes. The same occurs in the presence of Fe_2O_3 , which due to its strong catalytic oxidation activity for Hg^0 in flue gas, contributes to the concentration of mercury in fly ashes [33].

Arsenic in coal is normally associated with pyrite or other sulfides [29, 36]. During combustion, arsenic mostly volatilizes in the forms of $AsCl_3$ and AsO_2 , depending on the chlorine content in the coal [36]. According to Zheng *et al.* (2018), the presence of Cl in coal contributes to emission of As , while the presence of S inhibits this emission [33]. The presence of Fe or Ca results in the formation of $FeAsO_4$ or $Ca_3(AsO_4)_2$ on the surface of fly ash. Studies indicate that 0.2-52% of arsenic emitted as gas is in the form of As_2O_3 . As^{3+} corresponds to 10% of arsenic in fly ashes [33, 36, 37].

Zinc and cadmium appear in coal mainly in the form of sphalerite. Zinc has low volatility, leading to concentration mainly in the bottom ash and fly ash, and can be found in the forms of $2ZnO \cdot SiO_2$, $ZnO \cdot Fe_2O_3$ and $ZnO \cdot Al_2O_3$. Cadmium, on the other hand, volatilizes during combustion. With the cooling of flue gas the gaseous cadmium compounds, such as $CdCl_2$, condense below $580^\circ C$, forming particulates [36].

In coal, lead is mainly associated with organic compounds. It volatilizes at approximately $850^\circ C$ in the form of $PbO_{(g)}$. Between $730^\circ C$ and $820^\circ C$, it can be transformed into $PbO_{(s)}$ and below $730^\circ C$, solid lead sulfate is formed. The presence of chlorine can result in the Pb remaining in the form of vapor [36]. On the other hand, most of the chromium in coal is associated with clay minerals content in the inorganic matter. Cr enriches in the ash due to crystallization of Cr_2O_3 and the interaction of chromium with hematite. In pulverized coal combustion, the high concentration of toxic Cr^{6+} in fly ash requires attention [36].

TEs can be emitted as fly ash or volatiles, but emissions as fly ash are lower due to the high efficiency of removal with Electrostatic Precipitators (ESPs) or fabric filters (FF). On the other hand, gaseous emissions are more efficiently retained when Flue Gas Desulfurization (FGD) is present [29, 31]. Flue gas from coal-fired power plants are generally cleaned by selective catalytic reduction (SCR) for $deNO_x$, low-temperature electrostatic precipitators (LLT-ESP) / electric fabric filter (EFF), wet flue gas

desulphurization (WFGD) and wet electrostatic precipitators (WESP) [31, 34, 35]. Each pollution control system shows different results in the retention of each specific element [10]. ESP can retain 99.8% of the PM demonstrating high efficiency in retaining the TEs enriched in these particles. The elements emitted in gaseous form are retained mainly in the FGD. As an example, mercury was 49.6% removed in ESP and 80% in FGD, reaching a total removal of 89.92% [31]. Other factors also affect the TE emission in coal-fired power plants. Washing coal before combustion can remove 30 to 60% of TE [10], thereby reducing the overall emissions [30, 34], while the presence of chlorine increases the formation of metal chlorides, favoring the emission of TEs [32].

2.2.2 Combustion processes of sewage sludge

Emission of TEs has also been extensively studied in the processes of combustion of sewage sludge, municipal waste and industrial waste [4, 38-45]. These products can be used as fuel alone or in a co-combustion with another fuel [40]. Several studies have analyzed the concentration of trace elements in sewage sludge (Table 2.2). It can be seen that the concentration of trace elements in sewage sludge is high, especially for Cu and Zn, when compared with trace elements present in coal [41].

Table 2.2 – Summary of the concentrations of TEs in diverse sewage sludge samples in g/t of dry solid sewage sludge [3, 40, 42, 43].

TE	Sweden	Netherlands	Germany	Italy	Belgium	Hangzhou China	South China
Cr	33.00	113.00	91.00	240 - 650	85	196.67	198.1
Mn	280.00	546.00	-	75 - 98	-	-	-
Co	6.20	8.70	-	-	-	-	-
Ni	20.00	83.00	39.00	36 - 53	38.7	48.33	-
Cu	390.00	406.00	330.00	243 - 599	300	-	181.5
Zn	550.00	1349.00	1318.00	2796 - 4231	1581	1083.33	-
As	4.70	8.40	-	-	10.5	-	-
Cd	1.20	3.80	3.80	14 - 23	4.5	2.67	2.80
Sb	2.40	4.10	-	-	-	-	-
Pb	33.00	260.00	159.00	104 - 137	162	138.33	3.80
Hg	1.10	3.30	2.70	-	1.1	-	1.48
Se	1.30	2.40	-	-	-	-	-
V	18.00	24.00	-	-	-	-	-

Yang *et al.* (2015) studied the co-combustion of sewage sludge with coal gangue and its environmental implications. Since both residues are available in abundance and are both potential energy sources, they were tested as alternative energy sources [41, 42]. It was observed that As, Pb and Zn are the trace elements with the greatest volatilization potential during sewage sludge combustion. Since the coal gangue is composed mostly of kaolinite, its presence during the combustion of sewage sludge helped to retain trace elements, especially Pb and Zn [41].

Zhang *et al.* (2013) investigated the emission and distribution characteristics through a mass balance of Hg, Cd, Pb, Cr and Cu during co-combustion of sewage sludge in a pulverized coal fired power plant. They found that approximately 97% of Hg and 96% of Cd were distributed in fly ash and flue gas during the process. Most of the Cd was detected in the fly ash, making it easier to remove from the raw gas, while the majority of the Hg was present in the flue gas. Pb was distributed with approximately 40% in fly ash and 20% in the flue gas. Cr and Cu showed only a small amount in the fly ash and almost nothing in the flue gas, with more than 90% concentrated in bottom ash [42]. Additionally, by increasing the concentration of chlorine in the input, the distribution of the trace elements in fly ash and flue gas increased, with a consequent increment of emissions [42].

In another study, Van de Velden *et al.* [3] analyzed the distribution of Hg, As, Cd, Cu, Pb, Cr, Ni and Zn during fluidized bed combustion of sewage sludge. They found among the elements studied only Hg does not concentrate on the fly ash collected by ESP and a remarkable amount of Hg, Cd and Pb was also identified in the stack emissions. In fixed bed municipal solid waste incineration the effect of chlorine and calcium oxide on the volatility of Cd and Pb was studied by Wang *et al.* [44]. During incineration without the presence of chlorine, the reducing atmosphere provided the transformation of Pb and Cd monoxides into elemental substances and sulfides causing the volatilization of these elements at temperatures between 600 - 700 °C. CdO was more easily reduced than PbO, but the volatilization of PbO started before CdO when combusted in air. The addition of Cl in the mixture increased the volatilization of both elements and the addition of CaO had no impact on their volatility above 700 °C. To minimize the emission of these elements, it was suggested the elimination of reducing atmosphere conditions in Cl-free incineration or the addition of CaO for combustion at temperatures below 700 °C.

2.2.3 Ironmaking and Steelmaking

In the iron and steelmaking industry extensive amounts of gaseous and particle emissions are generated, especially fine particles where the main trace elements are enriched [22, 46]. According to Li *et al.* [47], the Iron and Steel Industry are responsible for 27% of airborne dust emission in China. In addition to iron ore sintering, discussed in more detail in the next section, other steps in the iron and steelmaking are relevant in for emission of trace elements, such as coke-making, blast furnace and BOF converter processes.

Tsai *et al.* [48] evaluated the emission of particulates and their composition in four processes of an integrated steel plant (coke-making, sintering, cold forming, and hot forming) in Taiwan, while Machemer [49] characterized the airborne and bulk particulate material from a blast furnace (BF) and a basic oxygen furnace (BOF) in Maryland, United States. Table 2.3 presents a summary of the results found by these authors.

Regarding the TEs, chromium, titanium and vanadium showed higher concentration in BOF particulates. Aluminum, zinc, nickel and arsenic were detected in high amounts in particulates from cold forming. In the particles emitted during iron ore sintering, lead, cadmium and selenium were identified in higher content than the other processes, while the highest amount of copper was detected in the hot rolling particles [48, 49].

Mercury is the most studied trace element of the iron and steel industry emissions due to its high volatility and insolubility in water. Between the raw materials, the iron concentrates are the major source of Hg (followed by coking coal), consequently, sinter and pellet plants are the major emitters of this element in the steel industry [46, 50]. In 2015, these processes were responsible for the emission of 15.9 t of Hg in China, followed by the blast furnace with 7.9 t. Coke ovens and roasting plants emitted together 7.0 t in the same year, while oxygen steelmaking generated less than 2.0 t [46].

Mercury can be emitted in a gaseous state, as Hg^0 or Hg^{2+} , or in a solid-state as particulate (Hg^p). According to Pacyna and Pacyna [51] and Pirrone *et al.* [52], the emission of Hg^0 , Hg^{2+} and Hg^p in the iron and steelmaking processes follow the approximate proportion of 80%, 15% and 5%, respectively [51, 52]. However, according to Xu *et al.* [53] and Wang *et al.* [54], the Hg^{2+} was found as the predominant specie in the emissions of these processes.

Table 2.3 – Elemental composition in mg/g of particulates emitted by the stages of the steelmaking process [48, 49].

TE	Coke making ^a	Sintering ^a	BF ^b	BOF ^b	Cold forming ^a	Hot forming ^a
Al	2.837	4.276	1	6.5	8.778	5.29
As	0.125	0.075	NA ^c	NA	0.37	0.203
B	NA	NA	0.005	0.02	NA	NA
Ba	1.417	0.075	ND	0.061	1.603	0.16
Bi	NA	NA	0.035	ND ^d	NA	NA
Ca	6.793	15.819	0.7	56.05	32.222	13.592
Cd	0.097	1.336	0.008	0.025	1.178	0.073
Co	0.001	0.007	0.024	0.015	0.24	0.035
Cr	ND	0.211	0.182	0.846	0.523	0.182
Cu	0.119	1.154	0.073	0.155	0.62	7.953
Fe	17.657	54.573	635.667	257.5	130.722	52.833
K	9.806	157.207	8.333	ND	25.056	8.099
Li	NA	NA	0.005	0.005	NA	NA
Mg	0.956	1.387	0.447	25.5	3.889	1.611
Mn	0.13	0.483	4.207	12.85	4.352	0.685
Na	11.715	31.51	NA	NA	33.333	40.702
Ni	0.225	0.631	0.13	0.065	20.98	0.769
P	NA	NA	0.477	0.98	NA	NA
Pb	0.292	22.882	ND	0.15	0.814	1.452
S	51.943	42.12	7.733	1.3	146.944	60.036
Sb	0.004	0.003	0.04	ND	0.003	0.511
Se	0.068	0.398	NA	NA	0.157	ND
Si	NA	NA	5.907	17.65	NA	NA
Sn	NA	NA	0.004	0.02	NA	NA
Sr	0.032	0.056	ND	0.039	0.005	0.024
Te	NA	NA	0.2	ND	NA	NA
Ti	NA	NA	0.207	1.27	NA	NA
V	ND	ND	0.075	0.201	ND	0.02
Y	NA	NA	ND	0.002	NA	NA
Zn	1.892	4.631	2.377	3.695	9.427	5.684

^a Composition of particulate emitted in processes of an integrated steel plant in Taiwan found by Tsai *et al.* [48].

^b Composition of the airborne and bulk particulate material from a BF and a BOF found by Macheimer [49].

^c NA: Not analyzed

^d ND: Not detected

2.3 Iron ore sintering

Iron ore agglomeration is the first step of the steel production in an integrated steel mill and the sintering process represents the vast majority installed in these plants, while the pelletization process is commonly found in the iron ore mining companies. Sintering is a thermal agglomeration process (1,300-1,480°C) [55] of a mixture of iron ore mineral fines (0.5-8 mm), by-products of the iron and steelmaking industry, fluxes, slag-forming elements and fossil fuel (coke), aiming to produce a ferrous burden (12-35 mm) for the blast furnace with the suitable physico-chemical and mechanical properties [56].

The sintering raw materials are firstly mixed in a granulation process, which conducts their homogenization in a mixing drum with water addition (6-8%). Dwight-Lloyd is the most used iron ore sintering machine in the world. It operates continuously by a series of pallets where the granulated sinter mix is loaded forming a bed height of 500-600 mm, which is subjected to the ignition on the top by oil or gas burners. Following, an air suction system promotes the formation of a narrow combustion zone (flame front) moving downwards (10-30 mm/min) and heating the mixture to 1,250-1,350 °C [56]. In a series of reactions a semi-molten material is produced and then cooled into several mineral phases of different chemical and morphological compositions (hematite, magnetite, ferrites and gangue composed mostly of calcium silicates). Moreover, ahead of the combustion zone, water evaporates and volatile substances are driven off by the wind boxes below the strand, which are connected to a fan via a gas scrubbing system. Finally, the sintered material is discharged and subjected to a final cooling, crushing and screening. Figure 2.1 shows a schematic flowchart of the process [57].

Figure 2.2 shows the temperature profile and the atmosphere regime of the sintering bed. The heating time at the high-temperature zone (above 1,100 °C) is around 1.5 min under a low partial oxygen pressure (pO_2) due to coke combustion and the cooling time (to 1,100 °C) must vary from 3 to 5 min in a condition of high partial oxygen pressure [57].

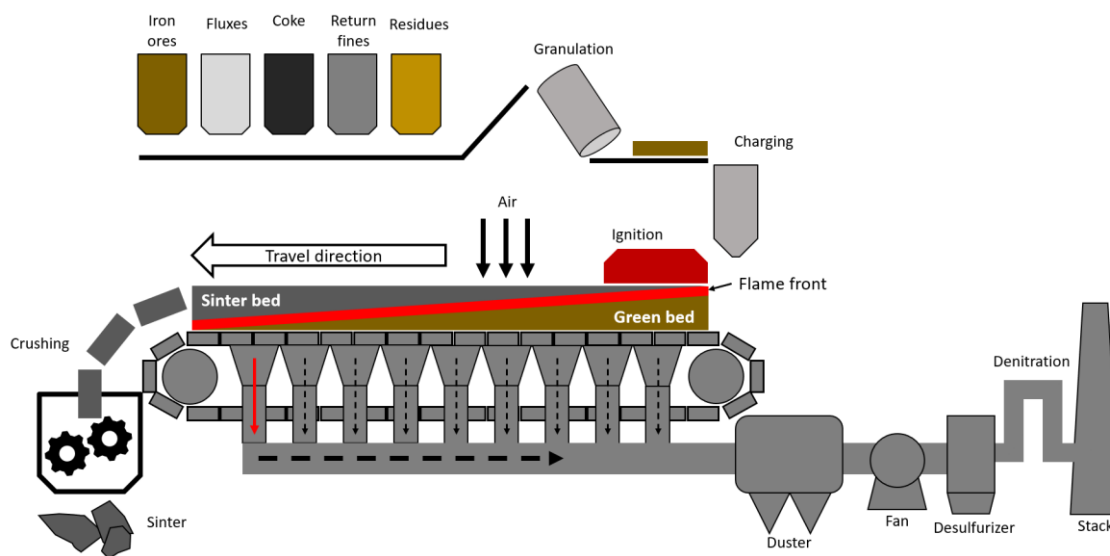


Figure 2.1 - Schematic diagram showing the material flow in a sinter plant (adapted from Wielgosinski and Łechtańska [58]).

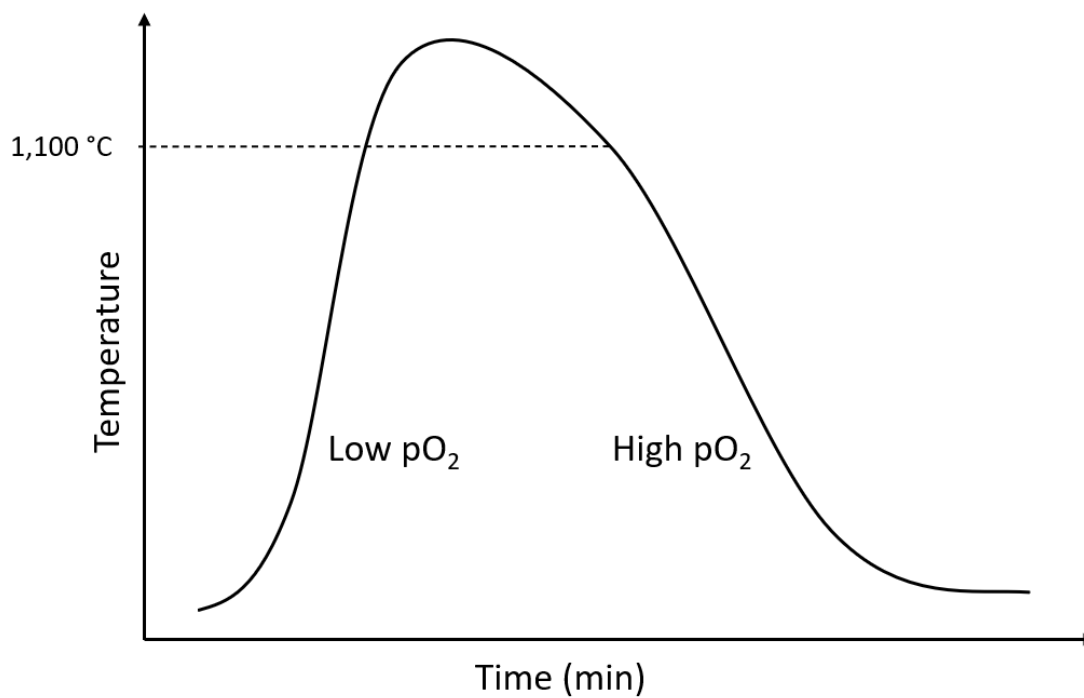


Figure 2.2 - Temperature profile and the atmosphere regime of the sintering bed (adapted from Cores *et al.* [57]).

2.3.1 Iron ore sintering air pollutants

The volume of gas emitted by a sintering plant ranges from 1,500 to 2,500 Nm³/t of graded sinter, depending on the operational conditions and plant size [26]. The off-gas contains carbon monoxide, carbon dioxide, sulfur and nitrogen oxides, alkali chlorides, hydrogen chloride, hydrogen fluoride, hydrocarbons, PAH (polycyclic aromatic hydrocarbons), PCDD/F (polychlorinated dibenzo-p-dioxins/dibenzofurans), PCBs (polychlorinated biphenyls) and heavy metals [59].

Greenhouse gases play an important role in the warming of the earth. The main greenhouse gas related to sintering is CO₂, with sintering accounting for approximately 7 to 9% of direct emissions from the use of fossil fuels (1.85 t CO₂ per ton of steel produced) [60]. SO_x and NO_x are other important pollutants emitted in the sintering process, which can cause acid rain and a series of respiratory and other diseases [59]. Iron ore sintering is responsible for approximately 3% of the total emission of NO_x in China [61].

Iron ore sintering is known as an important source of organic pollutants, such as PCDD/Fs (polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans) and PAH (Polycyclic Aromatic Hydrocarbons) which presents a high health risk due to its high toxicity and carcinogenic risk. [26, 59, 62]. According to Li *et al.* [63], sinter plants are responsible for about 30% of total PCDD/F to the atmosphere in stack gases in China. They studied the emission factors for some organic compounds in stack emissions from six Chinese iron ore sintering plants and found 2.47, 0.61, 552, 0.32, and 107 µg.t⁻¹ for PCDD/F, PCB, PCN (polychlorinated naphthalenes), PBDD/F (polybrominated dibenzo-p-dioxins/dibenzofurans) and PBDE (polybrominated diphenyl ethers) respectively.

PM (particulate matter) is another important air pollutant emitted by sintering plants [59]. Due to its small dimension and high surface area, it is also capable of directly depositing in the lung's alveoli, causing a series of respiratory diseases due to the concentration of toxic elements [22, 64]. The sintering process is the main PM emitter within an integrated steel plant [65], Gan *et al.* [66] attributed approximately 45% of the total Steelmaking PM emission to this process.

Another pollutant emitted by iron ore sintering that deserves special attention is heavy metals since they have long residence times in the atmosphere and are easily assimilated by natural organisms [7]. In addition to heavy metals emitted in PM, some of them can also be emitted as gas, such as Pb and Hg [26, 46]. As heavy metals are part

of the trace elements, the emission of these elements will be better discussed in a specific chapter.

2.3.2 Source of trace elements in the iron ore sintering process

The sintering mixture is composed of a wide variety of raw materials with the most diverse properties and chemical composition, which vary according to the input source, processing, transport and storage stages that precede sintering [20, 50].

In addition to iron ore, the sintering mixture is also composed of solid fuel (coke), slag-forming elements and fluxes (especially limestone, quick-lime and dolomite), returned fines (sinter with granulometry < 5 mm), and steel-making residues (like blast furnace, sinter and coke plant dust) [20, 50]. In our previous study, diverse iron ore sintering inputs were chemically characterized regarding the trace elements [50]. Table 2.4 presents a summary of these data in comparison with the results obtained by other authors.

Iron ores contain the largest concentrations of As, V and Hg. Coke breeze have the highest concentrations of Ni, Cr and Ti. The other elements did not show any clear pattern of concentration in one of the components of the sintering mixture. Considering a typical sintering mixture (61% of iron ore, 12% of fluxes, 23% of return fines and 4% coke breeze) [68] and the concentrations of trace elements presented in Table 2.4, it can be observed that iron ore is the main carrier of the trace elements. For example, Xu et al. [53] evaluated the supply of mercury in three different Chinese sintering and found between 74.84 and 92.22% of the mercury originating in iron ore.

2.3.3 The behavior of trace elements

During the iron ore sintering process trace elements can have four different destinations: remain in the sinter product, be retained by the abatement methods in the form of particulates, be emitted into the atmosphere as particulate material, or be emitted into the atmosphere in the gaseous form [6]. Figure 2.3 presents a schematic diagram of these possible paths of trace elements in the iron ore sintering process.

Table 2.4 – Trace element composition of iron ore sintering raw materials in ppm [22, 50, 53, 65-67].

Raw material	TE	Lau et al. [50]	Fan et al. [67]	Gan et al. [66]	Ji et al. [65] and Ji et al. [22]	Xu et al. [53]
Iron Ores (Sinter feed)	As	10.34	-	-	-	-
	Cd	0.11	-	-	-	-
	Cr	45.08	-	-	-	-
	Cu	16.88	-	-	-	-
	Ni	16.43	-	-	-	-
	Pb	7.47	60	62.0	120	-
	Cl	140.28	140	152.0	270	-
	Ti	-	-	-	564	-
	V	57.93	-	-	-	-
	Zn	20.08	-	-	350	-
	Hg	0.08	-	-	-	2.327x10 ⁻² - 4.997x10 ⁻²
Fluxes	As	2.93	-	-	-	-
	Cd	0.16	-	-	-	-
	Cr	45.29	-	-	-	-
	Cu	15.13	-	-	-	-
	Ni	15.06	-	-	-	-
	Pb	5.04	30 - 60	25.0 - 62.0	0	-
	Cl	106.57	110 - 150	107.0 - 152.0	30 - 120	-
	Ti	-	-	-	0 - 66	-
	V	6.57	-	-	-	-
	Zn	14.29	-	-	20 - 40	-
	Hg	0.02	-	-	-	0 - 3.100x10 ⁻³
Return fines	As	6.40	-	-	-	-
	Cd	0.16	-	-	-	-
	Cr	83.00	-	-	-	-
	Cu	11.30	-	-	-	-
	Ni	16.90	-	-	-	-
	Pb	12.80	60	55.0	80	-
	Cl	120.00	70	68.0	40	-
	Ti	-	-	-	528	-
	V	37.00	-	-	-	-
	Zn	113.00	-	-	240	-
	Hg	0.05	-	-	-	0 - 9.700x10 ⁻⁴
Coke breeze	As	4.17	-	-	-	-
	Cd	0.04	-	-	-	-
	Cr	148.00	-	-	-	-
	Cu	35.57	-	-	-	-
	Ni	135.87	-	-	-	-
	Pb	273.47	60	62.0	10	-
	Cl	6.67	150	149.0	580	-
	Ti	-	-	-	1200	-
	V	6.33	-	-	-	-
	Zn	63.67	-	-	40	-
	Hg	0.03	-	-	-	1.950x10 ⁻²

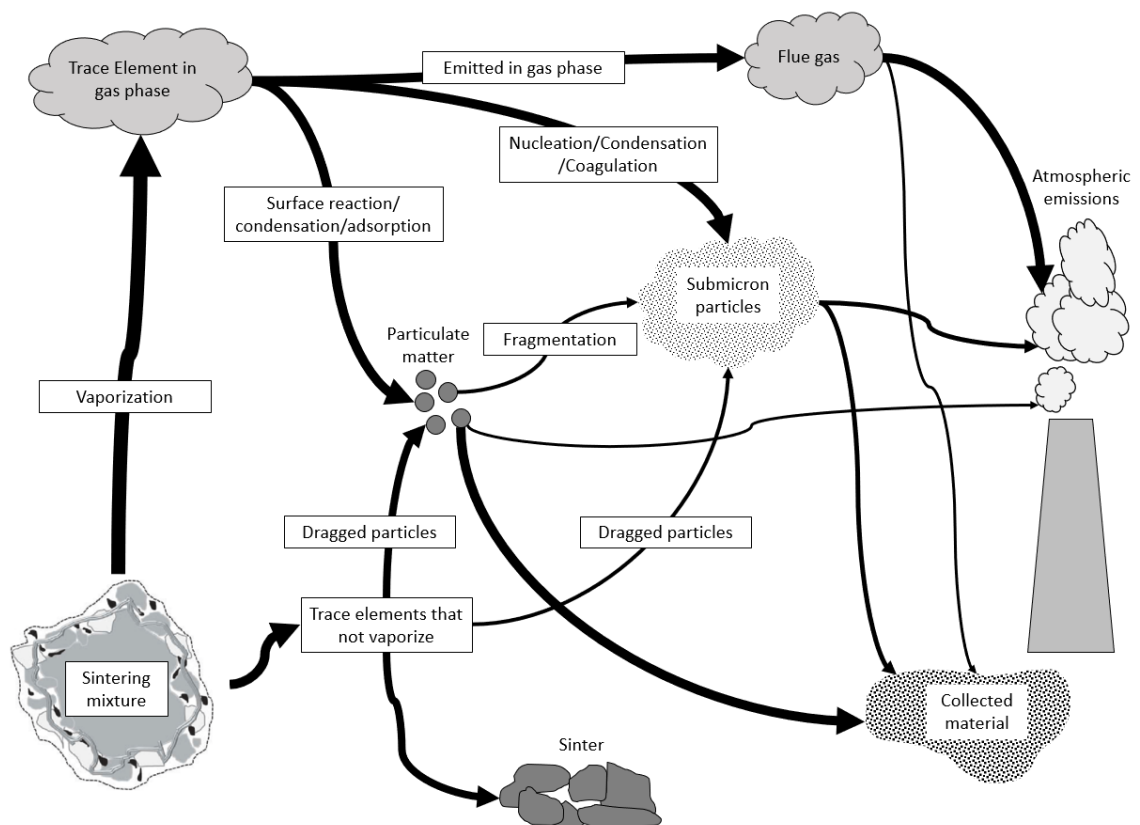


Figure 2.3 - Paths that trace elements can follow in iron ore sintering process (adapted from Xu *et al.* [6]).

Figure 2.4 shows the distribution of trace elements according to their volatility. In general, the trace elements are classified into three different classes in the combustion process [6, 30, 69]:

Class 1: Elements with low volatility index in the combustion processes, with a tendency to remain concentrated in the sinter or the coarse particles;

Class 2: Elements that can volatilize and condense during the combustion process. They are mainly concentrated in the PM, being enriched in the finer particles;

Class 3: Elements with low volatility temperature, being emitted mainly in their gaseous form.

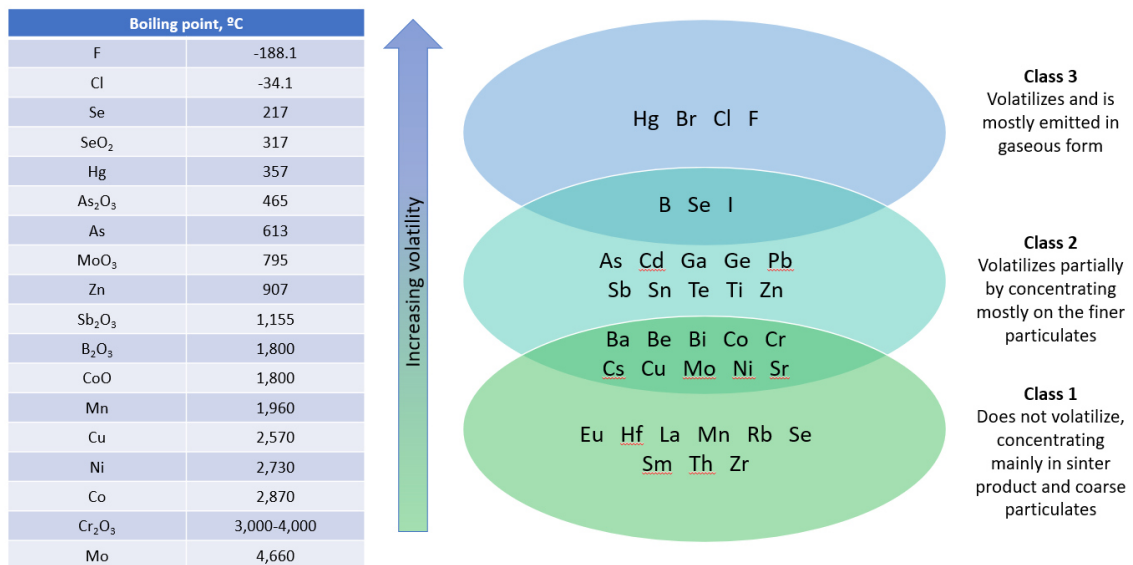


Figure 2.4 - Classification of trace elements based on their volatilization [6, 30, 69, 70].

Class 1 elements do not volatilize during the sintering process. In this way, these elements remain in the sinter cake or, the smaller particles can be dragged as particulate material, which is easily retained by the abatement systems [30]. Once the gases move away from the combustion front, the course of the vaporized trace elements (Classes 2 and 3) depends on whether or not these elements are converted into solid and/or liquid forms by physico-chemical phenomena [6]. These phenomena are:

- Heterogeneous condensation on surfaces or pre-existing particulate matter;
- Physical/chemical adsorption in pre-existing particulate material;
- Nucleation and coalescence as submicron particles in the presence of supersaturation;
- A chemical reaction between trace elements and constituents of the particulate material and flue gas;
- Remain in gaseous form for elements with a high vapor pressure at the exit temperatures of the gases.

According to Remus *et al.* [26], during the sintering process lead reacts to form volatile compounds (PbO-PbCl₂, PbCl₂, and, probably, PbCl₄). Thus, the emission of lead is related to the presence of chlorine in the sinter feed. Deng *et al.* [71] studied the correlation of lead emission and the presence of chlorine in coal in Chinese thermoelectric plants and found an *r*-value (Pearson correlation coefficient) of 0.7952.

This result can be transported to the iron ore sintering process, agreeing with Remus *et al.* [26] proposition. Besides, depending on the fluorine content in iron ores, lead fluorides can also be formed, being even more volatile and contributing to the emission of lead. In the higher temperature zones, zinc volatilizes and then reacts to form zinc ferrites. These ferrites can remain in the sinter or in the form of particulates, which can be collected relatively easy by the sintering abatement systems [26].

Cadmium, in its elemental form, has a volatilization temperature of 767 °C and should volatilize during the sintering process [70]. On the other hand, if the formation of CdO occurs, volatilization should only occur at 1,559 °C [70]. Furthermore, in the presence of Al and Si, CdO can form CdO.l₂O₃ and CdSiO₃, with both compounds being stable between 600 and 1,100 °C, retaining most of the cadmium in the solid form [72].

Arsenic, whether present in its elemental form or as As₂O₃, has a low boiling temperature and should volatilize during sintering [70]. On the other hand, some compounds stable at higher temperatures can be formed, such as FeAsO₄ (stable up to 1,100 °C), and AlAsO₄ (stable up to 1,400 °C). It is still possible, although unlikely, that Cd₃(AsO₄)₂, a stable compound up to approximately 1,200 °C, is formed by the interaction of As with Cd [73].

Regarding copper volatilization, the participation of chlorine is essential, since the boiling point of elemental copper is 2,560 °C [70]. In addition to allowing the volatilization of Cu due to the formation of CuCl₂, interactions of copper and chlorine have a major impact on the emissions of chlorinated aromatics. Copper acts as a catalyst in the formation of these compounds where the catalytic activity of CuCl₂·2H₂O is higher than elementary Cu for the *De Novo* formation (one of the main formation pathways of chlorinated aromatics) [74]. Concerning the formation of chlorobenzenes (CBzs) the catalytic activity is CuCl₂·2H₂O > Cu₂O > Cu > CuSO₄ > CuO and CuCl₂·2H₂O > Cu₂O > CuO > Cu > CuSO₄ for polychlorinated biphenyls (PCBs) [75].

Nickel and its main compounds have a high boiling point, indicating low emissions of this element. If nickel is emitted, it occurs by volatilization through the NiCl₂ formation, which sublimates at a temperature of 985 °C [70]. Guangxu *et al.* [76] analyzed the concentration of trace elements in the soil of an abandoned iron and steel factory in China and found that nickel concentration in soil was comparable to the background concentration of this element in the earth's crust. The low deposition of nickel in the soil is considered a consequence of a low air emission. These results agree with those

obtained by Zhao *et al.* [77], who studied the PM emitted at different points in a sintering plant and found a low nickel concentration in the PM of the sintering strand.

As in other high-temperature processes, mercury can be emitted in iron ore sintering as Hg^{2+} , Hg^0 , or Hg_p . Xu *et al.* [53] studied mercury emissions in three different Chinese sintering plants and found a high proportion of Hg^{2+} at the inlet of ESP (64.36 - 94.72%), followed by Hg^0 and, to a lesser extent, Hg_p . Wu *et al.* [78] found similar results, with approximately 70% of Hg^{2+} , 30% of Hg^0 , and no Hg_p in Chinese iron ore sintering emissions in 2015. The high proportion of Hg^{2+} can be explained since Fe_2O_3 has significant catalytic activity in the oxidation of Hg in the presence of Cl [79, 80].

Fan *et al.* [67] studied the concentration of Pb, K, Na, Cl, and S in $\text{PM}_{2.5}$ emitted in a laboratory-scale sinter pot test. It was identified that the concentration of these elements is significantly higher in the $\text{PM}_{2.5}$ collected after the increase of flue gas temperature (stage-2) than before (stage-1). The presence of these elements in Fe-rich and Fe-Si-Al-rich particles was further detected, as well as the formation of CaSO_4 in both stages, while the PbCl_2 -KCl, KCl, and NaCl in the stage-2 [67].

2.3.4 Trace elements emissions factors

The emission factor is the average emission rate of a given source related to units of production or process. In atmospheric emissions from iron ore sintering, the emission factor corresponds to a mass of the pollutant emitted by mass of sinter produced.

Table 2.5 presents the results reported by Remus [26] and Passant *et al.* [81] who evaluated the emission factors of trace elements in iron ore sintering. The values obtained show significant variation, which can be explained by the different properties of the raw materials employed and the different abatement systems of each sintering plant evaluated. Lead presents the highest emission factor, which can reach 5,661.2 mg/t of sinter. However, great variability of emission factors was found for the same element in different sintering plants. The least variable was Se with a variation of 7.15 times between the highest and lowest emission factors.

2.3.5 Measurements used in studies/industry

A complete atmospheric study requires sample collection over long periods and covering a large area, making these studies expensive and complex to perform. An widely

adopted alternative is the use of organisms that act as bio-accumulators [82]. Rahayu [83] proposed the use of a wild plant (*Eichhornia crassipes*) as a bioaccumulation agent for Pb, Fe, Hg, Zn, Cu and Cd. According to Loppi, *et al.* [84] some lichen species can be used for the same purpose. The latter used lichen *Parmelia Caperata (L.) Ach.* as a bio-accumulator to evaluate the atmospheric contamination of Cd, Cr, Cu, Hg, Ni, Pb and Zn. Holy *et al.* [85] evaluated the mosses as bio-accumulators of Cd, Hg and Pb, finding strong correlations between the concentrations of Cd and Pb in mosses and sampling site-specific and regional characteristics. There are other studies that are also pointing out on several species that can be used as bio-accumulators for heavy metals [86-90].

Table 2.5 - Trace elements emission factor in iron ore sintering (mg/t sinter) [26, 81].

Element	Remus (2013)	Passant et al. (2002)
As	0.6 - 15	6.2
Cd	0.2 - 276.7	32.0
Cr	3.6 - 125.1	5.5
Cu	1.9 - 600.5	183.4
Hg	0.1 - 207	18.3
Mn	3.4 - 539.4	110.0
Ni	1.3 - 175.6	8.2
Pb	26.1 - 5,661.2	3,136.4
Se	21.8 - 120.5	155.9
Tl	0.5 - 86.6	48.6
V	0.6 - 58.5	1.8
Zn	2.1 - 1931.3	255.8

Continuous emission monitoring systems can be used for some pollutants, but they are not yet commercially viable for trace elements, therefore measurements are performed manually [30]. Trace element sampling is performed using isokinetic methods. A probe/pitot is used in the duct orifice with a vacuum pump to adjust the sampling flow to isokinetic conditions. The sampled gas passes through a hot box and a cyclone and/or filter where the particles are collected. The gas then flows through impingers with a series of oxidizing agents to collect the trace elements present in the gas. This method has several limitations and is an expensive procedure, which requires a long time for collection to obtain significant results. Moreover, it does not present punctual results over time, only the average of emissions over the collection period, and, in general, needs approximately one day for analysis and results [30]. Technologies towards the online

measurement of trace element emissions were not developed yet. According to Nalbandian [30], the solution seems to be based on spectroscopy, where the most promising technologies are: Atomic Fluorescence Spectroscopy, Atomic Absorption Spectroscopy, and Tunable Diode Laser Absorption Spectroscopy.

2.3.6 Air Pollution Control Devices (APCD) employed / available

The atmospheric emissions abatement system installed in iron ore sintering has diverse configurations and equipment, each having its advantages and disadvantages. Among the various equipment that can be used alone or in combination are the Electrostatic Precipitators (ESP), Fabric Filters (FF), Cyclones, Flue Gas Desulfurization (FGD) and Selective Catalytic Reduction (SCR), although no equipment is specific for the removal of trace elements [26, 46]. Each of these equipment are described in detail.

Electrostatic Precipitator (ESP)

The most common equipment for treating flue gas from sintering plants is ESP. This equipment works by generating an electrostatic field in the dust path. A voltage of thousands of volts is applied ionizing the gas around the electrodes. The negative ions flow to the plates charging the particles in the gas stream, causing them to be attracted to the grounded plates. In dry ESPs the plates go through a mechanical stirring process, causing the particles to fall into the collectors. In the wet ESPs, a constant flow of water removes the particles, and the liquid obtained is treated later [26, 30, 91].

ESPs reduce dust emissions by more than 95%, in some cases reaching reductions of more than 99% [26, 30]. They have good efficiency for particles with specific resistivity is in the range of 10^4 to 10^9 Ωm . In general, the particles in the sintering flue gas fall in this range, but in some compounds, such as alkali chlorides, heavy metal chlorides and calcium oxides, the specific resistivity may be greater than the appropriate range, making their removal difficult [26]. Also, since they are more difficult to charge, ESPs are less efficient with fine and ultra-fine particles, where the semi-volatile trace elements tend to concentrate [30].

Several technologies can increase the efficiency of ESPs. Remus *et al.* [26] highlighted three of them:

- Use of energy pulse superimposition: the pulse system provides high voltage pulses at a frequency of up to 200 pulses per second. This technique helps to energize

particles with high resistivity, providing a better charging of particles and distribution of current in the precipitator;

- Moving Electrode Electrostatic Precipitator (MEEP): in this equipment, several electrode plates move during operation, being cleaned continuously by rotating brushes. This prevents the formation of insulating dust layers that adversely affect the operation of the ESP;
- Electrostatic Space Cleaner Super (ESCS): this equipment works with high voltages and greater distance between the electrodes.

Fabric filter (FF)

In FF the particulate material is removed from the flue gas by passing through a system of filter bags. The collected dust forms a porous cake on the surface of the filters where it also acts as an additional filtering layer [30]. During the filtration process, a series of reagents can be used to increase the removal of other pollutants besides dust, such as HCl, HF, SO_x, PCDD/F, PCB, HCB and PAH. The particulates accumulated on the filter are removed, being partially recirculated in the waste gas to increase the efficiency of the adsorbents. The remaining dust can be disposed and/or recirculated in the sintering strand [26].

In general, the filtering process takes place with the following steps: injection of adsorbents (lignite coke, active carbon and zeolites) to reduce the emission of hazardous compounds; injection of NaHCO₃ or slacked lime to reduce acidic emissions; capture of dust in the filter element; dust removal from the filter element; recirculation of part of the collected dust; use of an exhaust fan to extract the filtered gas [26].

Although they can be used in isolation, in iron ore sintering the FFs are usually used in combination with the cyclone [26, 30, 46]. The use of FF with ESP increases the retention of particulate material and ultra-fine particles, directly impacting the retention of trace elements, especially semi-volatile elements [35, 92]. According to Nalbandian [30], fabric filters can achieve an efficiency of 99.95% in the collection of particles of all sizes and more than 99% efficiency for fine particles.

Cyclones

Cyclones are used mainly as a pre-treatment of gases. Since they are based on inertia, they are efficient only for the retention of coarse particles. More than one cyclone can be used in series, increasing efficiency for particles of different sizes. Its main function is to protect the following equipment from the abrasion generated by the larger particles [26].

Wet Fine Scrubber

Scrubbers are devices that remove particulate material from the flue gas using a liquid. Since the particles emitted by iron ore sintering are relatively fine and contain hydrocarbons, a special wet fine scrubber is required [26]. AIRFINE is one model of wet fine scrubber, which consists of two steps of work. The first step is responsible for cooling the waste gas by spraying a solution of NaOH in water on the surface of the scrubber. In the next stage, the fines are washed by injecting a mist of water and compressed air into the gas flow, removing fine particles, including heavy metal chlorides. The collected liquid is treated and recirculated in the process [26].

Other models of wet fine scrubbers are electrostatic or ionizing advanced wet scrubbers or condensing wet scrubbers [30]. Electrostatically enhanced wet scrubbers apply a charge to the particulate material, collecting it through neutral or negatively charged electrodes. In a condensing wet scrubber, the flue gas is cooled below its adiabatic saturation temperature, causing the condensation of a large fraction of elements that are in the vapor phase. Besides, cooling induces condensation of water vapor, forming droplets that assist in the collection of fine particulate matter [6].

Some trace elements of greater volatility and, consequently, more difficult to remove by ESP and FF, can be removed in the wet fine scrubber due to water solubility. This is the case for mercury in the form of Hg^{2+} [92]. According to Zhang *et al.* [35], other examples of trace elements that can be removed in wet fine scrubbers are As, Cr and Pb.

Flue Gas Desulfurization (FGD)

Desulfurization can be achieved wet or dry. Wet desulfurization is carried out through the wet fine scrubber with the addition of Ca or Mg as reagents, forming CaSO_4 or MgSO_4 . The residues from this process, such as gypsum, magnesium sulfate and ammonium hydrogen sulfite (NH_4HSO_3), are treated and recirculated or reused in other processes, such as cement production. This process also helps to remove HCl, HF and dust from the flue gas, but does not affect emissions of NO_x [26].

Dry desulfurization is achieved through the adsorption of SO_2 on activated carbon. The waste gas flow is directed to an activated carbon bed, where several pollutants are adsorbed. In addition to SO_2 , this process removes HCl, HF, Hg^{2+} , dust, PCDD/F and, if ammonia is injected into the gas before the catalytic bed, NO_x . As a co-product, sulfuric acid (H_2SO_4) can be obtained [26].

Selective Catalytic Reduction

A catalytic reduction process can be used for the control of NO_x emissions. In this process vanadium pentoxide (V₂O₅) or tungsten oxide (WO₃) on titanium oxide (TiO₂) carrier can be applied as catalysts, where NO_x is reduced by ammonia or urea to N₂ and H₂O. The proper operating temperature is between 300 and 400 °C, making it necessary to reheat the gas before the process [26].

SCR is beneficial for Hg⁰ oxidation, in which hydrogen chloride (HCl) and sulfur dioxide (SO₂) have positive effects. On the other hand, the literature does not offer much information about the efficiency of the SCR in controlling the emission of other TEs [9].

APCDs configurations and efficiency in retaining trace elements

An iron ore sintering plant may have several combinations of control equipments described above as APCD. According to Xu *et al.* [53], a typical configuration is the use of ESP, FF and FGD. These authors evaluated the efficiency of mercury removal in three sintering plants with the following APCD configurations:

- (1) ESP, circulating fluidized-bed flue gas desulphurization (CFB-FGD) and FF
- (2) ESP and dense flow absorber flue gas desulphurization (DFA-FGD)
- (3) ESP and ammonia flue gas desulphurization (AFGD)

The results obtained showed removal of mercury between 97.5 and 98.3%, which is the best result for the configuration (2) [53].

Although there are not many studies evaluating the efficiency of APCDs for the removal of trace elements in sintering, there are many of that evaluated the efficiency of APCDs in coal-fired power plants [9, 34, 93]. Attalla *et al.* [93] accessed the efficiency of ESP, FF, and FGD in controlling trace element emissions of a conventional pulverized coal plant with results shown in Table 2.6.

In general, a high retention capacity of most trace elements can be observed in the evaluated equipment. The elements that presented the greatest difficulty in retention were B, Cd, Cu and, especially, the most volatile Hg and Se. ESP, FF and FGD showed efficiency greater than 95% for all other elements.

Comparing the results found by Xu *et al.* [53] and Attalla *et al.* [93] it is possible to observe a much higher mercury retention capacity in the sintering process than in coal-fired power plants. This can be explained by the higher concentration of Hg²⁺ in the sintering gas. According to Ghorishi and Sedman [94], Hg²⁺ tends to be adsorbed on particulates

and is partially removed by the ESP. Besides, FGD has a greater capacity for removing Hg^{2+} , since it is more reactive and water-soluble [53].

Table 2.6 - Trace element control efficiencies in different APCD technologies in % of retention [93].

Trace element	ESP	FF	FGD
Sb	96	97	99
As	98.5	98.6	98.7
Ba	99.5	98	99.5
Be	98.5	98.6	98.7
B	68	97	63
Cd	83	94	96
Cr	97.5	99.5	99.5
Co	98	99	99
Cu	89	99.5	99
Pb	98	98.5	99
Mn	97	99.5	99.5
Hg	30	60	20
Mo	96	100	99
Ni	96	99	99
Se	21	65	60
V	98	100	99.5

Zhu *et al.* [34] evaluated several combinations of APCD concerning the ability to remove trace elements from emissions of coal-fired power plants in China. The following range of technologies were proposed, individually or in combination: ESP, FF, WFGD, SCR, SNCR (selective non-catalytic reduction) and SMC (a special mercury control technology, like activated carbon injection (ACI), bromide injection into the furnace (BIF), oxidation catalysts, low-temperature mercury capture, the thief carbon process, etc.). From the results obtained, as presented in Table 2.7, the best configurations are SCR + SMC + ESP + WFGD and SCR + FF + WFGD.

In another study, Zhao *et al.* [9] evaluated the emissions of Zn, Sb, Pb, Cd, As, Cr, Mn and Ba in a Chinese coal-fired power plant equipped with SCR, ESP, and WFGD. The efficiency of removing the eight elements until the ESP was between 99.43 and 99.95%. The WFGD increased the efficiency to between 99.78 and 99.96%, retaining 18.10% of Sb, 22.25% of Ba, 23.16% of Cr, 28.39% of Mn, 31.15% of As, 53.17% of Pb, 61.26% of Zn, and 68.47% of Cd.

Table 2.7 - Trace elements removal efficiency of 7 different APCD combinations in coal-fired power plants in China [34].

APCD combination	Co-benefit removal efficiency (%)							
	Hg	As	Se	Pb	Cd	Cr	Ni	Sb
ESP	33.17	86.20	73.78	97.16	96.46	98.53	93.52	83.5
ESP+WFGD	71.41	97.29	93.41	99.39	99.31	99.79	98.70	97.1
SCR+ESP+WFGD	74.82	97.29	93.41	99.39	99.31	99.79	98.70	97.1
SNCR+ESP+WFGD	71.41	97.29	93.41	99.39	99.31	99.79	98.70	97.1
SCR+SMC+ESP+WFGD	97.48	97.29	93.41	99.39	99.31	99.79	98.70	97.1
FF	67.92	99.00	65.00	99.00	97.63	95.13	94.83	94.3
FF + WFGD	86.28	99.80	91.20	99.78	99.54	99.32	98.97	99
SCR + FF + WFGD	87.91	99.80	91.20	99.78	99.54	99.32	98.97	99

Font *et al.* [95] evaluated the retention capacity of trace elements by the APCDs of two coal-fired power plants in Spain. High efficiency of ESP was found in the retention of most of the elements, but Hg, Cl, F, As, Se and B showed volatile behavior, making retention by ESP difficult. For these elements, the FGD acted with high retention efficiency for gaseous Cl, F, and B (> 95%), As (78-90%), Se (84-94%), and relatively high for Hg (64 -74%).

As can be seen, the removal of elements that are not in the vapor phase (Classes 1 and 2) is carried out mainly by dust collectors and the biggest challenge is the removal of elements with high volatility. An alternative to remove these elements would be to force their condensation through the gas cooling, collecting them as particles. However, in this case, there is a need to reheat the gas before the stack makes the process less economically viable [6]. The use of sorbent injection to capture these elements is also an interesting alternative, which has led to some studies [94, 96-98].

Yao and Naruse [96] proposed the use of compounds based on silica and calcium as sorbents to capture Pb, Cd and Cr during solid fuel combustion. The tested sorbents based on their order of efficiency in retaining Pb and Cd were kaolin, zeolite, limestone, scallop, mullite, apatite, bauxite and lastly silica.

For the retention of mercury, activated carbon is widely used and can be efficient in adsorbing other trace elements, such as As [99]. Ghorishi and Sedman [94] suggest Ca-based sorbents to control total mercury emissions and found that the most effective sorbents are those with significant surface area and pore volume. Moreover, Lineberry *et al.* [98] proposed the use of palladium-decorated carbon as a substrate for mercury capture and found promising capabilities, with total efficiencies greater than 90% in laboratory-scale tests and in the order of ~60% in a real industrial flue gas.

2.4 Conclusions

This paper reviews the emission of trace elements in the iron ore sintering process, focusing on the source of the elements, their behavior under high temperature industrial conditions, and the devices employed to control emissions. Moreover, processes with similar characteristics, such as coal-fired power plants, were explored to assist in understanding the behavior of the trace elements in sintering plants. The mechanisms of emission of trace elements proved to be complex and their control can be performed through the appropriate choice of raw materials. Due to the availability, cost and desired quality, it is not always possible to adjust the raw materials, thus requiring a greater investment in air pollution control devices. Iron ore is the main responsible raw material for input trace elements in the sintering process due to the amount of iron ore in the sintering mixture. In general, these elements undergo a series of physicochemical transformations throughout the process and may remain in the solid-state, volatilize during burning and recondense in APCD or remain in the gaseous state during the flue gas treatment. Most trace elements are retained in APCD in the form of particulates, but volatile and semi-volatile elements (As, Se, Hg, Cd, etc) can remain as gases or concentrate in the finer particulates, making them difficult to remove by conventional methods of controlling particulate emissions. Modern technologies (e.g the use of activated carbon or other sorbents) have demonstrated high efficiency in removing the volatile and semi-volatile elements from the flue gas. The risks associated with the emission of these elements and the still incipient knowledge about their behavior during iron ore sintering makes evident the need for further studies.

2.5 Acknowledgments

The authors express gratitude to CAPES-PROEX, CNPq, and FAPEMIG for the accomplishment and support of this work.

2.6 References

- [1] S.A.M. Nimir, Environmental impact of some trace elements emission from the work environment of Atbara Cement Factory and Atbara Railway Foundry, 2006.
- [2] I. Filizok, A. Uğur Görgün, Atmospheric depositional characteristics of ^{210}Po , ^{210}Pb and some trace elements in İzmir, Turkey, *Chemosphere* 220 (2019) 468-475.

- [3] M. Van de Velden, R. Dewil, J. Baeyens, L. Josson, P. Lanssens, The distribution of heavy metals during fluidized bed combustion of sludge (FBSC), *Journal of Hazardous Materials* 151(1) (2008) 96-102.
- [4] C.-L. Lin, S.-H. Chang, T.-H. Peng, Investigation on the Emission of Heavy Metals in Fluidized-Bed Incineration during the Agglomeration/Defluidization Process, *Energy & Fuels* 24(5) (2010) 2910-2917.
- [5] Y. Sekine, K. Sakajiri, E. Kikuchi, M. Matsukata, Release behavior of trace elements from coal during high-temperature processing, *Powder Technology* 180(1) (2008) 210-215.
- [6] M. Xu, R. Yan, C. Zheng, Y. Qiao, J. Han, C. Sheng, Status of trace element emission in a coal combustion process: a review, *Fuel Processing Technology* 85(2) (2004) 215-237.
- [7] C. Boente, N. Matanzas, N. García-González, E. Rodríguez-Valdés, J.R. Gallego, Trace elements of concern affecting urban agriculture in industrialized areas: A multivariate approach, *Chemosphere* 183 (2017) 546-556.
- [8] C.L. Senior, Development of a mechanistic model for prediction of emission of trace elements from coal-fired power plants, *Fuel Processing Technology* 63(2) (2000) 75-77.
- [9] S. Zhao, Y. Duan, C. Li, Y. Li, C. Chen, M. Liu, J. Lu, Partitioning and Emission of Hazardous Trace Elements in a 100 MW Coal-Fired Power Plant Equipped with Selective Catalytic Reduction, Electrostatic Precipitator, and Wet Flue Gas Desulfurization, *Energy & Fuels* 31(11) (2017) 12383-12389.
- [10] H. Tian, K. Liu, J. Zhou, L. Lu, J. Hao, P. Qiu, J. Gao, C. Zhu, K. Wang, S. Hua, Atmospheric Emission Inventory of Hazardous Trace Elements from China's Coal-Fired Power Plants—Temporal Trends and Spatial Variation Characteristics, *Environmental Science & Technology* 48(6) (2014) 3575-3582.
- [11] C.O.T.E.U. European Parliament, Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, in: C.O.T.E.U. European Parliament (Ed.) *Official Journal of the European Union*, 2008, pp. 169 - 212.
- [12] U.S. EPA (U.S. Environmental Protection Agency), National primary and secondary ambient air quality standards for lead., (2008).

- [13] U.S. EPA (U.S. Environmental Protection Agency), National primary ambient air quality standards for PM_{2.5}, 2013.
- [14] B. Siciliano, G. Dantas, C.M.d. Silva, G. Arbilla, The Updated Brazilian National Air Quality Standards: A Critical Review, *Journal of the Brazilian Chemical Society* 31 (2020) 523-535.
- [15] M.o.E.P.o. China, Ambient air quality standard, 2012.
- [16] W.H.O. WHO, WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, World Health Organization, Geneva, Switzerland, 2005.
- [17] W.H.O. WHO, WHO Expert Consultation: Available evidence for the future update of the WHO Global Air Quality Guidelines (AQGs), World Health Organization, Copenhagen, Denmark, 2015.
- [18] X. Zhou, V. Strezov, Y. Jiang, X. Yang, T. Kan, T. Evans, Contamination identification, source apportionment and health risk assessment of trace elements at different fractions of atmospheric particles at iron and steelmaking areas in China, *PLOS ONE* 15(4) (2020) e0230983.
- [19] World Steel Association, Global crude steel output increases by 3.4% in 2019, World Steel Association, Brussels, Belgium, 2020, p. 3.
- [20] D. Fernández-González, I. Ruiz-Bustanza, J. Mochón, C. González-Gasca, L.F. Verdeja, Iron Ore Sintering: Raw Materials and Granulation, *Mineral Processing & Extractive Metallurgy Review* 38(1) (2017) 36-46.
- [21] L. Lu, O. Ishiyama, 14 - Iron ore sintering, in: L. Lu (Ed.), *Iron Ore*, Woodhead Publishing 2015, pp. 395-433.
- [22] Z. Ji, X. Fan, M. Gan, Q. Li, X. Chen, Y. Tian, T. Jiang, Speciation of PM_{2.5} Released from Iron Ore Sintering Process and Calculation of Elemental Equilibrium, *ISIJ International* 57(4) (2017) 673-680.
- [23] G.M. Olmez, F.B. Dilek, T. Karanfil, U. Yetis, The environmental impacts of iron and steel industry: a life cycle assessment study, *Journal of Cleaner Production* 130 (2016) 195-201.
- [24] Y. Chen, Z. Guo, Z. Wang, Influence of CeO₂ on NO_x emission during iron ore sintering, *Fuel Processing Technology* 90(7) (2009) 933-938.

- [25] G.C. Abreu, J.A.d. Carvalho, B.E.C.d. Silva, R.H. Pedrini, Operational and environmental assessment on the use of charcoal in iron ore sinter production, *Journal of Cleaner Production* 101 (2015) 387-394.
- [26] R. Remus, M.A. Aguado, S. Roudier, L. Delgado, Best Available Techniques (BAT) Reference Document for Iron and Steel Production, Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), European Commission (Joint Research Centre, Institute for Prospective Technological Studies), Seville (Spain), 2013.
- [27] N. Menad, H. Tayibi, F.G. Carcedo, A. Hernández, Minimization methods for emissions generated from sinter strands: a review, *Journal of Cleaner Production* 14(8) (2006) 740-747.
- [28] BP, BP Statistical Review of World Energy 2019, London, 2019.
- [29] S. Zhao, Y. Duan, H. Tan, M. Liu, X. Wang, L. Wu, C. Wang, J. Lv, T. Yao, M. She, H. Tang, Migration and Emission Characteristics of Trace Elements in a 660 MW Coal-Fired Power Plant of China, *Energy & Fuels* 30(7) (2016) 5937-5944.
- [30] H. Nalbandian, Trace element emissions from coal, IEA Clean Coal Centre, 2012.
- [31] R. Meij, H. te Winkel, The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations, *Atmospheric Environment* 41(40) (2007) 9262-9272.
- [32] D. Pudasainee, J.-H. Kim, S.-H. Lee, J.-M. Park, H.-N. Jang, G.-J. Song, Y.-C. Seo, Hazardous air pollutants emission from coal and oil-fired power plants, *Asia-Pacific Journal of Chemical Engineering* 5(2) (2010) 299-303.
- [33] C.-h. Zheng, L. Wang, Y.-x. Zhang, W.-g. Weng, H.-t. Zhao, J.-s. Zhou, X. Gao, Co-benefit of hazardous trace elements capture in dust removal devices of ultra-low emission coal-fired power plants, *Journal of Zhejiang University-SCIENCE A* 19(1) (2018) 68-79.
- [34] C. Zhu, H. Tian, K. Cheng, K. Liu, K. Wang, S. Hua, J. Gao, J. Zhou, Potentials of whole process control of heavy metals emissions from coal-fired power plants in China, *Journal of Cleaner Production* 114 (2016) 343-351.
- [35] C. Zheng, L. Wang, Y. Zhang, J. Zhang, H. Zhao, J. Zhou, X. Gao, K. Cen, Partitioning of Hazardous Trace Elements among Air Pollution Control Devices in Ultra-Low-Emission Coal-Fired Power Plants, *Energy & Fuels* 31(6) (2017) 6334-6344.

- [36] S. Zhao, Y. Duan, Y. Li, M. Liu, J. Lu, Y. Ding, X. Gu, J. Tao, M. Du, Emission characteristic and transformation mechanism of hazardous trace elements in a coal-fired power plant, *Fuel* 214 (2018) 597-606.
- [37] H.Z. Tian, L. Lu, J.M. Hao, J.J. Gao, K. Cheng, K.Y. Liu, P.P. Qiu, C.Y. Zhu, A Review of Key Hazardous Trace Elements in Chinese Coals: Abundance, Occurrence, Behavior during Coal Combustion and Their Environmental Impacts, *Energy & Fuels* 27(2) (2013) 601-614.
- [38] B. Fu, G. Liu, M.M. Mian, C. Zhou, M. Sun, D. Wu, Y. Liu, Co-combustion of industrial coal slurry and sewage sludge: Thermochemical and emission behavior of heavy metals, *Chemosphere* 233 (2019) 440-451.
- [39] L. Mu, L. Peng, X. Liu, H. Bai, C. Song, Y. Wang, Z. Li, Emission Characteristics of Heavy Metals and Their Behavior During Coking Processes, *Environmental Science & Technology* 46(11) (2012) 6425-6430.
- [40] L.E. Åmand, B. Leckner, Metal emissions from co-combustion of sewage sludge and coal/wood in fluidized bed, *Fuel* 83(13) (2004) 1803-1821.
- [41] Z. Yang, Y. Zhang, L. Liu, X. Wang, Z. Zhang, Environmental investigation on co-combustion of sewage sludge and coal gangue: SO₂, NO_x and trace elements emissions, *Waste Management* 50 (2016) 213-221.
- [42] G. Zhang, J. Hai, M. Ren, S. Zhang, J. Cheng, Z. Yang, Emission, Mass Balance, and Distribution Characteristics of PCDD/Fs and Heavy Metals during Cocombustion of Sewage Sludge and Coal in Power Plants, *Environmental Science & Technology* 47(4) (2013) 2123-2130.
- [43] R. Wang, Z. Zhao, Q. Yin, J. Liu, Mineral transformation and emission behaviors of Cd, Cr, Ni, Pb and Zn during the co-combustion of dried waste activated sludge and lignite, *Fuel* 199 (2017) 578-586.
- [44] X. Wang, Y. Huang, C. Liu, S. Zhang, Y. Wang, G. Piao, Dynamic volatilization behavior of Pb and Cd during fixed bed waste incineration: Effect of chlorine and calcium oxide, *Fuel* 192 (2017) 1-9.
- [45] Z. Wang, C. Hong, Y. Xing, Y. Li, L. Feng, M. Jia, Combustion behaviors and kinetics of sewage sludge blended with pulverized coal: With and without catalysts, *Waste Management* 74 (2018) 288-296.

- [46] Z. Yang, B. Gong, J. Yang, Y. Zhao, J. Zhang, 6 - Trace element partition in a coal-feed industry furnace, in: Y. Zhao, H. Li, J. Yang, J. Zhang, C. Zheng (Eds.), *Emission and Control of Trace Elements from Coal-Derived Gas Streams*, Woodhead Publishing 2019, pp. 173-226.
- [47] M. Li, H. Liu, G. Geng, C. Hong, F. Liu, Y. Song, D. Tong, B. Zheng, H. Cui, H. Man, Q. Zhang, K. He, Anthropogenic emission inventories in China: a review, *National Science Review* 4(6) (2017) 834-866.
- [48] J.-H. Tsai, K.-H. Lin, C.-Y. Chen, J.-Y. Ding, C.-G. Choa, H.-L. Chiang, Chemical constituents in particulate emissions from an integrated iron and steel facility, *Journal of Hazardous Materials* 147(1) (2007) 111-119.
- [49] S.D. Machemer, Characterization of Airborne and Bulk Particulate from Iron and Steel Manufacturing Facilities, *Environmental Science & Technology* 38(2) (2004) 381-389.
- [50] L.L. Lau, L.F.A. de Castro, F.d.C. Dutra, M.V. Cantarino, Characterization and mass balance of trace elements in an iron ore sinter plant, *Journal of Materials Research and Technology* 5(2) (2016) 144-151.
- [51] E.G. Pacyna, J.M. Pacyna, Global Emission of Mercury from Anthropogenic Sources in 1995, *Water, Air, and Soil Pollution* 137(1) (2002) 149-165.
- [52] N. Pirrone, P. Costa, J.M. Pacyna, R. Ferrara, Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region, *Atmospheric Environment* 35(17) (2001) 2997-3006.
- [53] W. Xu, M. Shao, Y. Yang, R. Liu, Y. Wu, T. Zhu, Mercury emission from sintering process in the iron and steel industry of China, *Fuel Processing Technology* 159 (2017) 340-344.
- [54] F. Wang, S. Wang, L. Zhang, H. Yang, W. Gao, Q. Wu, J. Hao, Mercury mass flow in iron and steel production process and its implications for mercury emission control, *Journal of Environmental Sciences* 43 (2016) 293-301.
- [55] T.C. Eisele, S.K. Kawatra, A REVIEW OF BINDERS IN IRON ORE PELLETIZATION, *Mineral Processing & Extractive Metallurgy Review* 24(1) (2003) 1.
- [56] D. Fernández-González, I. Ruiz-Bustanza, J. Mochón, C. González-Gasca, L.F. Verdeja, Iron Ore Sintering: Process, *Mineral Processing and Extractive Metallurgy Review* 38(4) (2017) 215-227.

- [57] A. Cores, L. Verdeja, S. Ferreira, I. Ruiz-Bustinza, J. Mochón, Iron ore sintering. Part 1. Theory and practice of the sintering process, *Dyna* (Medellin, Colombia) 80 (2013) 152.
- [58] G. Wielgosinski, P. Łechtańska, The use of ammonium sulfate as an inhibitor of dioxin synthesis in iron ore sintering process, *Ecological Chemistry and Engineering. S = Chemia i Inżynieria Ekologiczna. S 21* (2014) 59-70.
- [59] D. Fernández-González, I. Ruiz-Bustinza, J. Mochón, C. González-Gasca, L.F. Verdeja, Iron Ore Sintering: Environment, Automatic, and Control Techniques, *Mineral Processing & Extractive Metallurgy Review* 38(4) (2017) 238-249.
- [60] World Steel Association, STEEL'S CONTRIBUTION TO A LOW CARBON FUTURE AND CLIMATE RESILIENT SOCIETIES, World Steel Association, 2020.
- [61] X. Fan, Z. Yu, M. Gan, X. Chen, Q. Chen, S. Liu, Y. Huang, Elimination Behaviors of NO_x in the Sintering Process with Flue Gas Recirculation, *ISIJ International* 55(10) (2015) 2074-2081.
- [62] U. Quaß, M. Fermann, G. Bröker, The European Dioxin Air Emission Inventory Project—Final Results, *Chemosphere* 54(9) (2004) 1319-1327.
- [63] S. Li, G. Liu, M. Zheng, W. Liu, J. Li, M. Wang, C. Li, Y. Chen, Unintentional production of persistent chlorinated and brominated organic pollutants during iron ore sintering processes, *Journal of Hazardous Materials* 331 (2017) 63-70.
- [64] A. Przybysz, A. Sæbø, H.M. Hanslin, S. Gawronski, Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time, *The Science of the total environment* 481C (2014) 360-369.
- [65] Z. Ji, X. Fan, M. Gan, X. Chen, Q. Li, Y. Tian, X. He, Y. Zhou, T. Jiang, Influence Factors on PM_{2.5} and PM₁₀ Emissions in Iron Ore Sintering Process, *ISIJ International* 56(9) (2016) 1580-1587.
- [66] M. Gan, Z. Ji, X. Fan, X. Chen, Q. Li, L. Yin, X. He, Y. Zhou, T. Jiang, Emission Behavior and Physicochemical Properties of Aerosol Particulate Matter (PM_{10/2.5}) from Iron Ore Sintering Process, *ISIJ International* 55(12) (2015) 2582-2588.
- [67] X. Fan, Z. Ji, M. Gan, Q. Li, X. Chen, T. Jiang, Participating patterns of trace elements in PM_{2.5} formation during iron ore sintering process, *Ironmaking & Steelmaking* 45(3) (2018) 288-294.

- [68] M. Gan, X.H. Fan, Z.Y. Ji, X.L. Chen, L. Yin, T. Jiang, Z.Y. Yu, Y.S. Huang, Optimising method for improving granulation effectiveness of iron ore sintering mixture, *Ironmaking & Steelmaking* 42(5) (2015) 351-357.
- [69] J.A. Ratafia-Brown, Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers, *Fuel Processing Technology* 39(1) (1994) 139-157.
- [70] W.M. Haynes, D.R. Lide, T.J. Bruno, *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 97th Edition, CRC Press, Boca Raton, Florida, 2016.
- [71] S. Deng, Y. Shi, Y. Liu, C. Zhang, X. Wang, Q. Cao, S. Li, F. Zhang, Emission characteristics of Cd, Pb and Mn from coal combustion: Field study at coal-fired power plants in China, *Fuel Processing Technology* 126 (2014) 469-475.
- [72] Z. Zhu, Y. Huang, J. Zha, M. Yu, X. Liu, H. Li, X. Zhu, Emission and Retention of Cadmium during the Combustion of Contaminated Biomass with Mineral Additives, *Energy & Fuels* 33(12) (2019) 12508-12517.
- [73] M.L. Contreras, J.M. Arostegui, L. Armesto, Arsenic interactions during co-combustion processes based on thermodynamic equilibrium calculations, *Fuel* 88(3) (2009) 539-546.
- [74] Y. Sun, L. Liu, X. Fu, T. Zhu, A. Buekens, X. Yang, Q. Wang, Mechanism of unintentionally produced persistent organic pollutant formation in iron ore sintering, *Journal of Hazardous Materials* 306 (2016) 41-49.
- [75] L. Liu, W. Li, Z. Xiong, D. Xia, C. Yang, W. Wang, Y. Sun, Synergistic effect of iron and copper oxides on the formation of persistent chlorinated aromatics in iron ore sintering based on in situ XPS analysis, *Journal of Hazardous Materials* 366 (2019) 202-209.
- [76] Z. Guangxu, Q. Guo, H. Xiao, T. Chen, J. Yang, Multivariate statistical and lead isotopic analyses approach to identify heavy metal sources in topsoil from the industrial zone of Beijing Capital Iron and Steel Factory, *Environmental Science and Pollution Research* 24 (2017).
- [77] L. Zhao, W. Sun, X. Li, Z. Ye, J. Huang, G. Zhang, J. Cai, Assessment of particulate emissions from a sinter plant in steelmaking works in China, *Environmental Monitoring and Assessment* 189(8) (2017) 368.

- [78] Q. Wu, W. Gao, S. Wang, J. Hao, Updated atmospheric speciated mercury emissions from iron and steel production in China during 2000–2015, *Atmos. Chem. Phys.* 17(17) (2017) 10423-10433.
- [79] G.E. Dunham, R.A. DeWall, C.L. Senior, Fixed-bed studies of the interactions between mercury and coal combustion fly ash, *Fuel Processing Technology* 82(2) (2003) 197-213.
- [80] S. Ghorishi, C. Lee, W. Jozewicz, J. Kilgroe, Effects of Fly Ash Transition Metal Content and Flue Gas HCl/SO₂ Ratio on Mercury Speciation in Waste Combustion, *Environmental Engineering Science - ENVIRON ENG SCI* 22 (2005) 221-231.
- [81] N.R. Passant, M. Peirce, H.J. Rudd, D.W. Scott, I. Marlowe, J.D. Watterson, UK Particulate and Heavy Metal Emissions from Industrial Processes, DEFRA, the National Assembly for Wales, the Scottish Executive and the Department of the Environment in Northern Ireland, 2002.
- [82] G.A. Abril, E.D. Wannaz, A.C. Mateos, R. Invernizzi, R.R. Plá, M.L. Pignata, Characterization of atmospheric emission sources of heavy metals and trace elements through a local-scale monitoring network using *T. capillaris*, *Ecological Indicators* 40 (2014) 153-161.
- [83] S.T. Rahayu, M. Faradilla, E.Y. Verawati, M. Triana, Respon Bioakumulator Eceng Gondok (*Eichhornia crassipes*) Terhadap Logam Berat Pb dan Cd di Sungai Pegangsaan Dua, *Pharmaceutical Sciences and Research (PSR)*; Vol 1, No 1 (2014) (2016).
- [84] S. Loppi, F. Chiti, A. Corsini, L. Bernardi, Lichen biomonitoring of trace metals in the Pistoia area (central northern Italy), *Environmental Monitoring and Assessment* 29(1) (1994) 17-27.
- [85] M. Holy, R. Pesch, W. Schröder, H. Harmens, I. Ilyin, R. Alber, Y. Aleksiyayenak, O. Blum, M. Coşkun, M. Dam, L. Temmerman, N. Fedorets, R. Figueira, M. Frolova, M. Frontasyeva, N. Goltsova, L. Gonzalez Miqueo, K. Grodzińska, Z. Jeran, S. Korzekwa, First thorough identification of factors associated with Cd, Hg and Pb concentrations in mosses sampled in the European Surveys 1990, 1995, 2000 and 2005, *Journal of Atmospheric Chemistry* 63(2) (2009) 109-124.
- [86] F.D. Bora, C.I. Bunea, R. Chira, A. Bunea, Assessment of the Quality of Polluted Areas in Northwest Romania Based on the Content of Elements in Different Organs of Grapevine (*Vitis vinifera* L.), *Molecules* 25(3) (2020) 750.

- [87] F. Gür, G. yaprak, Biomonitoring of metals in the vicinity of Soma coal-fired power plant in western Anatolia, Turkey using the epiphytic lichen, *Xanthoria parietina*, *Journal of Environmental Science and Health, Part A* 46(13) (2011) 1503-1511.
- [88] Satya, D.K. Upreti, D.K. Patel, *Rinodina sophodes* (Ach.) Massal.: a bioaccumulator of polycyclic aromatic hydrocarbons (PAHs) in Kanpur City, India, *Environmental monitoring and assessment* 184(1) (2012) 229-238.
- [89] A. Turkyilmaz, H. Sevik, M. Cetin, The use of perennial needles as biomonitors for recently accumulated heavy metals, *Landscape and Ecological Engineering* 14(1) (2018) 115-120.
- [90] M.C. Freitas, Elemental bioaccumulators in air pollution studies, *Journal of Radioanalytical and Nuclear Chemistry* 192(2) (1995) 171-181.
- [91] E. Guerriero, A. Lutri, R. Mabilia, M.C.T. Scianò, M. Rotatori, Polycyclic Aromatic Hydrocarbon Emission Profiles and Removal Efficiency by Electrostatic Precipitator and Wetfine Scrubber in an Iron Ore Sintering Plant, *Journal of the Air & Waste Management Association* 58(11) (2008) 1401-1406.
- [92] S. Zhao, Y. Duan, L. Chen, Y. Li, T. Yao, S. Liu, M. Liu, J. Lu, Study on emission of hazardous trace elements in a 350 MW coal-fired power plant. Part 1. Mercury, *Environmental Pollution* 229 (2017) 863-870.
- [93] M.I. Attalla, S. Morgan, K. Riley, G. Bryant, P.F. Nelson, Trace element deportment in combustion processes., Research report (Cooperative Research Centre for Coal in Sustainable Development (Australia)) ; 50., QCAT Technology Transfer Centre, Queensland, Australia, 2004, p. 84.
- [94] S.B. Ghorishi, C.B. Sedman, Low Concentration Mercury Sorption Mechanisms and Control by Calcium-Based Sorbents: Application in Coal-Fired Processes, *Journal of the Air & Waste Management Association* 48(12) (1998) 1191-1198.
- [95] O. Font, M. Izquierdo, R. Ochoa-González, C. Leiva, M.A. López-Antón, X. Querol, M. Díaz-Somoano, M. Martínez-Tarazona, C. Pereira, S. Rico, A. Tomás, P. Gomez, A. Gimenez Alonso, E. Alvarez, Fate of trace pollutants in PCC-FGD power plants, 3rd World of Coal Ash, WOCA Conference - Proceedings (2009).
- [96] H. Yao, I. Naruse, Using sorbents to control heavy metals and particulate matter emission during solid fuel combustion, *Particuology* 7(6) (2009) 477-482.

[97] P. Biswas, C.Y. Wu, Control of Toxic Metal Emissions from Combustors Using Sorbents: A Review, *Journal of the Air & Waste Management Association* 48(2) (1998) 113-127.

[98] Q.J. Lineberry, Y. Cao, Y. Lin, S. Ghose, J.W. Connell, W.-P. Pan, Mercury Capture from Flue Gas Using Palladium Nanoparticle-Decorated Substrates as Injected Sorbent, *Energy & Fuels* 23(3) (2009) 1512-1517.

[99] V.C. Pandey, J.S. Singh, R.P. Singh, N. Singh, M. Yunus, Arsenic hazards in coal fly ash and its fate in Indian scenario, *Resources, Conservation and Recycling* 55(9) (2011) 819-835.

Capítulo 3. Artigo B - Evaluation of Trace Elements Behavior in Iron Ore Sintering Process

M.Eng. Lucas Ladeira Lau^a M.Eng. Alei Leite Alcântara Domingues^b, Dr. Flavio de Castro Dutra^b, Dr. Valdirene Gonzaga de Resende^{b,*}, Dr. Maurício Covcevich Bagatini^a

^aPrograma de Pós-Graduação em Engenharia Metalúrgica, Materiais e de Minas, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil.

^bCentro de Tecnologia de Ferrosos, Vale, Nova Lima, Minas Gerais, Brazil.

**Corresponding author*

Abstract

The increasing concern over environmental issues, including more strict legislation around the world, requires improving the understanding of the flow of trace elements in consolidated processes of modern society. This work evaluated the behavior of seven trace elements (arsenic, cadmium, copper, nickel, lead, mercury, and chlorine) in the iron ore sintering process and their impact in atmospheric emissions. Six different sintering mixtures composed with different iron ores were submitted to the sintering pot test. Chemical characterization of the mixtures and the respective sinter obtained along with an atmospheric emission analysis was conducted. As and Cu were the major trace elements contained in the mixtures before sintering. In general, after tests trace elements exhibited a low tendency of concentrating on emissions, except for mercury. In emissions, these elements were majorly detected in solid particulates. The arsenic and lead emission increased in the presence of chlorine in the mixture, while the cadmium emission had a positive correlation with arsenic and iron content in the mixture.

Keywords: Sintering; Trace elements; Mass balance; Emissions

3.1 Introduction

The concern about the preservation of the environment and the control of factors that have an impact on human health is a worldwide tendency that results in increasingly more rigorous environmental legislation. The introduction of stringent regulations setting limits on emissions of some pollutants that were previously not controlled, such as trace elements and fine powdery, aroused consequently. The European legislation, for example, shows limits for the concentration of PM_{2.5} (Particulate Matter smaller than 2.5 micrometers), lead, arsenic, cadmium, and nickel in the air [1]. Other countries are making progress in their environmental legislation based on the European one. As an example there is China, that drastically reduced a series of emission limits, such as the particulate matter, decreasing from 150mg/Nm³ to 50mg/Nm³ [2]. These pollutants show a significant impact on the environment and human health, given that particulate matter has a small dimension, high surface area, and concentration of heavy metals and organic pollutants [3, 4].

TEs can behave in three different ways when subjected to high temperature processes. Some of them tend to remain in the solid state, such as V, Cr, Mn, Co and Ni. Other TEs are partially volatilized and can be recondensed in atmospheric pollutant control devices, such as Zn, Pb, Cd and As. However, some others volatilize, remaining in the vapor phase until emission into the atmosphere, for example Hg, F, Cl, Br [5, 6]. The elements that volatilize can be emitted in the form of gas or fine particles, mainly PM_{2.5}, being able to travel great distances in the atmosphere before depositing, contaminating the soil and water, and entering the food chain through vegetables and fish [7-10]. Some elements are chemically stable and tend to accumulate in human tissues and in the environment [1].

Due to more stringent, understanding the behavior of the trace elements in industrial processes becomes increasingly relevant. Since the steel industry works at high temperatures and with large amounts of different raw materials that elevate its polluting potential, the study of these emissions is of utmost importance for better process control. Amongst all the processes involved in the production of steel, sintering is the main emitter of pollutant gases and powdery materials that contain trace elements [11-14]. This process is responsible for approximately 45% of the total emissions of an integrated steel plant [15].

However, there are very few studies available regarding the behavior of trace elements in the steel industry. Tsai *et al.* [16] evaluate the chemical constituents, with TEs among

them, in particulate matter from an iron and steel facility. Xu *et al.* [17] and Wang *et al.* [18] studied the emission of mercury in the iron and steel industry. In our previous work, a chemical characterization of several typical sintering raw materials was conducted, aiming at identifying the origin of trace elements in this process [19]. In that study, the ferrous waste added in the mixture was identified as the raw material containing the highest concentration of trace elements in its composition. The trace elements that showed the greatest contribution in emissions during the sintering process were identified as zinc, chlorine, and lead. The present study aimed to evaluate the behavior of seven trace elements (arsenic, cadmium, copper, nickel, lead, mercury, and chlorine) in the iron ore sintering process and their impact in atmospheric emissions.

3.2 Materials and Methods

In the present work, seven trace elements (arsenic, cadmium, lead, chlorine, copper, mercury and nickel) were chosen to be studied in the iron ore sintering process considering the following criteria: (a) restrictions in environmental legislation, (b) mass contribution in sintering process, (c) tendency of these elements to concentrate in atmospheric emission, (d) participation of these elements in dioxins formation, and (e) concentration of these elements in the sinter feed.

3.2.1 Raw Materials

Eleven different iron ores were used to produce six industrial representative sintering mixture with lime, coke, calcitic and dolomitic limestone, quartzite, and return sinter. Table 3.1 shows the composition of these mixtures.

The mixtures were chemically characterized regarding the main components and trace elements evaluated in this work. The chemical analysis of total iron was carried out by volumetric titration and the determination of the loss on ignition was conducted with a thermogravimetric analyzer (Leco, model TGA 701). The preparation of the samples for quantitative chemical analysis of Si, Al, Ca, Mg, P, Ti, and Mn by atomic spectroscopy with plasma was based on the combination of the heated digestion system and the use of multiacids. This quantitative chemical analysis of metals was carried out in the ICP Varian 715 ES, with radial-view and ICP Expert II software.

Table 3.1 - Composition of sintering mixtures used in the tests (in mass percentage)

Raw Material	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5	Mixture 6
Sinter feed A	5.33	5.31	5.32	0.00	0.00	0.00
Sinter feed B	15.99	15.92	15.97	20.91	20.89	13.00
Sinter feed C	5.33	0.00	5.32	0.00	0.00	0.00
Sinter feed D	8.00	7.96	7.98	0.00	7.83	7.80
Sinter feed G	10.66	10.61	10.64	10.46	10.45	10.40
Sinter feed H	8.00	7.96	0.00	7.84	7.83	7.80
Sinter feed I	0.00	5.31	7.98	0.00	0.00	5.20
Sinter feed J	0.00	0.00	0.00	7.84	0.00	0.00
Sinter feed K	0.00	0.00	0.00	5.23	5.22	7.80
Dolomitic Limestone	5.46	5.96	5.45	3.43	3.40	3.46
Calcitic Limestone	5.15	4.98	5.12	8.97	9.09	9.21
Quartzite	0.09	0.00	0.21	0.00	0.10	0.17
Lime	2.00	2.00	2.00	1.32	1.32	1.32
Fuel	4.00	4.00	4.00	4.00	3.85	3.85
Return Sinter	30.00	30.00	30.00	30.00	30.00	30.00

For the characterization of arsenic, cadmium, chlorine, copper, lead, and nickel, samples of 0.25 g were pulverized, then digested in perchloric, nitric, and hydrofluoric acid. The residue was diluted after being leached out with diluted hydrochloric acid. The prepared sample was then submitted to analysis in the ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy) and ICP-MS (Inductively Coupled Plasma - Mass Spectrometry).

For the characterization of mercury, samples of 0.50 g were prepared, pulverized, and digested in aqua regia for 45 minutes in a graphite heating block. After cooling, the resultant solution was diluted to 12.5 mL in demineralized water. Part of the sample was treated with stannous chloride to reduce the mercury, which was then volatilized through a purge with argon and measured by AAS (Atomic Absorption Spectrometry).

3.2.2 Sintering tests

60 kg of the six mixtures were prepared according to the proportion shown in Table 3.1 and water was added up to reach moisture of 7.5%. The tests were conducted in a pilot sintering equipment (Sinter Pot Test), and its schematic diagram is shown in Figure 3.1. These apparatus present a cone-shaped pot with an inferior diameter of 270 mm and a superior diameter of 300 mm. The height of the bed can vary from 400 and 700mm and volume from 25.4 and 43.9L. For the test it was used a volume of 34,32L and a height of 550mm.

In these tests, firstly the mixture was loaded in the pot, and then a burner was used to promote the solid fuel ignition in the superior layer of the mixture. The flame front at approximately 1,280°C, moved downwards inside the bed, pushed by an airflow varying from 100 to 160 Nm³/h. At the end of the burning, the sinter cake was subjected to a drum mill and the sinter was separated from the return fines through sieving. For the test to be considered valid, the return fines mass generated should be equal to the loaded, allowing a variation of 2%.

The sinter and the return fines were weighed and chemically characterized using the same processes described for the characterization of the raw material. This process was repeated three times for each mixture.

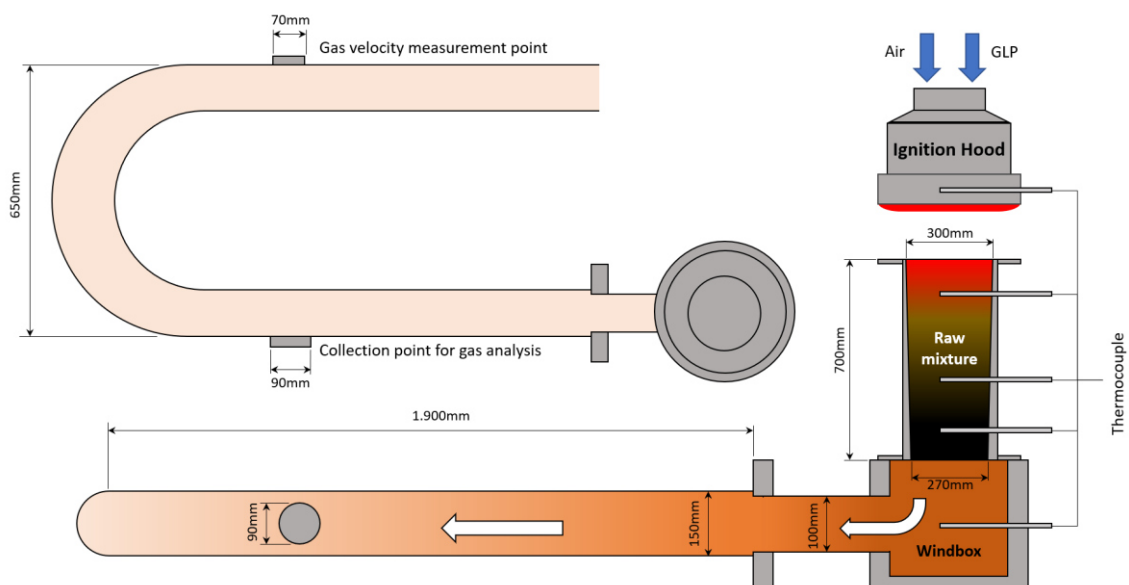


Figure 3.1 - Schematic representation of the pilot sintering used in the tests.

3.2.3 Trace elements evaluation

During the sinter pot tests, the analysis of the atmospheric emissions generated in the process was carried out to identify the emissions of trace elements. For this purpose, methodologies described in the methods of the U.S.EPA (U.S. Environmental Protection Agency) were employed (Method 1A, Method 2, Method 3, Method 4, and Method IO-3.3) [20, 21]. Due to the characteristics inherent to the sintering equipment used, an adaptation was made adopting a sampling time of 20 minutes. The equipment used to collect the gases was “Isokinetic equipment for monitoring gases and particulate materials - Model CIPA” produced by the company Energética-RJ. The equipment

operates with a probe, which is inserted into the exhaust duct and collects part of the emission gases. At another point, the pitot tube is inserted, which makes it possible to obtain the speed of the gas inside the duct. Figure 1 illustrates the gas collection point and the speed measurement point. The sampled gas goes through the hot box and the high-efficiency cyclone, where the largest particles are collected. After the cyclone the gas is filtered through a glass fiber filter, of high efficiency, collecting particles of a diameter greater than 0.3 micrometers. Next, the gas passes to the cold box where the impingers (washing bottles) are installed. In the first impingers, the gas is cooled and the condensable and water-soluble gaseous materials are removed. The other impingers remove the water present in the sampled gases. Finally, the material collected in the filters and washers was characterized and the concentration of the elements in the emission gases is calculated. The quantitative results obtained in the CIPA method have no absolute significance and it was used with the purpose of comparison between the studied mixtures.

From the concentration of trace elements in the mixtures and their respective sinter, as well as with the masses of each one, the recovery factor x_R and emission factor x_E were calculated through Eqs. (1) and (2), respectively.

$$x_R = \left(\frac{c_s \times m_s}{c_m \times m_m} \right) \times 100\% \quad \text{Eq. 1}$$

$$x_E = \left(1 - \frac{c_s \times m_s}{c_m \times m_m} \right) \times 100\% \quad \text{Eq. 2}$$

Where C_s and C_m are the trace elements concentration in the sinter and the mixture, respectively, and m_s and m_m are the respective masses of sinter and mixture.

The monotonic correlation between the chemical composition of raw materials and the emission factor of trace elements was evaluated by the Spearman's Correlation Method. This method was chosen since it is not possible to identify a normal distribution for the concentration of all the elements evaluated in the six mixtures, which means that Pearson's method cannot be used. A significance level (p-value) of 0.05 was adopted to validate the test. All the statistical analyzes were executed in the software Minitab 17.3.1.

3.3 Results and discussion

3.3.1 Sintering conditions

Table 3.2 shows the parameters obtained in each of the fires. As can be seen, similar sintering conditions were used for the 6 fires. Figure 3.2 shows the temperature profile used during the sinter pot test.

Table 3.2 – Sintering conditions.

Mixture	M1	M2	M3	M4	M5	M6
Moisture (%)	7.6	7.4	7.5			
Fuel (%)	4.0	4.0	3.9			
Loaded weight (kg)	57.2	56.8	57.2			
Cake weight (kg)	49.3	48.9	49.2			
Fines weight (kg)	15.6	15.6	15.6			
Time (min)	26.3	26.8	27.3			
Fines balance (%)	98.9	99.5	98.8			
Average dry density (t/m ³)	1.7	1.7	1.7			
Average wet density (t/m ³)	1.8	1.8	1.8			
Max temperature (°C)	1,200	1,199.7	1,188.3			
Bed productivity (t/m ² /24h)	27.7	26.8	26.7			
C.E.C kg/t sinter	68.4	68.8	66.8			

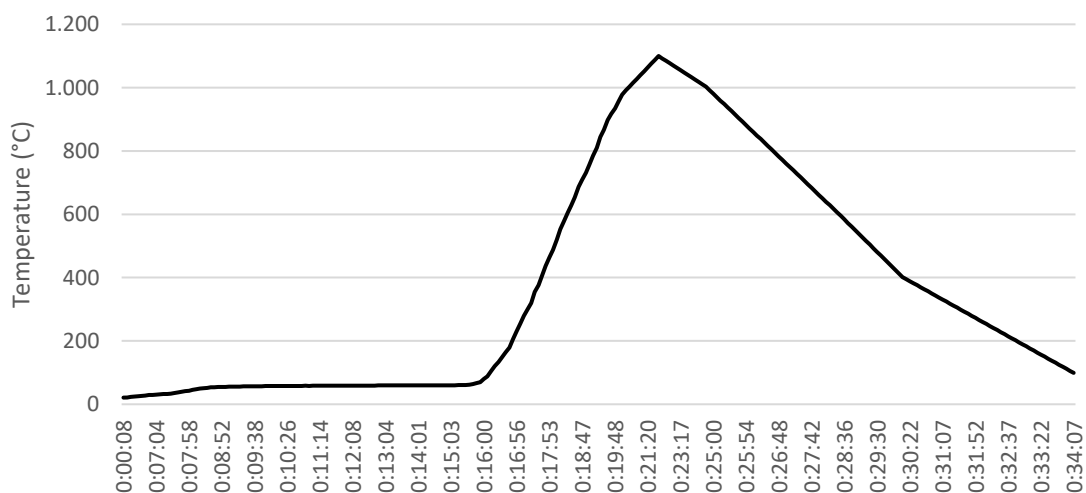


Figure 3.2 – Temperature profile of the sinter pot test.

3.3.2 Trace elements in the mixture

The chemical composition of the raw materials can vary a lot depending on their geology and extraction process, which added to the variation of the proportions in the mixtures, results in a wide variety of chemical compositions for the sintering mixtures [19, 22]. The chemical composition of the mixtures used in this study is shown in Table 3.3.

The mixtures 1 and 3 presented a higher level of trace elements, corresponding to 157.12 and 131.92 ppm, respectively. Considering the proportion of the raw materials (Table 3.1) and the chemical composition of the mixtures, it is noted that the addition of sinter feed C results in an elevated concentration of arsenic, which causes a great impact on the total concentration of trace elements.

Table 3.3 - Chemical characterization of the mixtures used in the tests.

Component	M 1	M 2	M 3	M 4	M 5	M 6
Fe (%)	49.83	49.70	49.92	49.28	48.81	49.24
FeO (%)	1.41	0.02	1.40	0.04	0.05	0.07
SiO ₂ (%)	4.88	4.86	4.87	5.00	5.04	5.07
Al ₂ O ₃ (%)	1.43	1.41	1.40	1.24	1.41	1.35
P (%)	0.12	0.12	0.12	0.12	0.12	0.12
Mn (%)	0.16	0.16	0.16	0.18	0.15	0.17
CaO (%)	8.79	8.75	8.76	9.52	9.56	9.64
MgO (%)	1.47	1.47	1.47	1.05	1.04	1.05
TiO ₂ (%)	0.42	0.41	0.41	0.08	0.08	0.08
PPC (%)	7.76	8.03	7.66	8.41	8.86	8.18
As (ppm)	59.80	8.40	60.20	9.80	11.70	9.30
Cd (ppm)	0.19	0.04	0.19	0.04	0.05	0.05
Cu (ppm)	33.90	21.80	31.80	24.50	28.20	30.60
Ni (ppm)	16.70	12.30	15.70	8.20	9.20	9.60
Pb (ppm)	16.50	6.90	14.00	7.00	7.30	7.70
Hg (ppm)	0.03	0.04	0.03	0.06	0.08	0.05
Cl (ppm)	30.00	10.00	10.00	20.00	30.00	30.00
Total trace elements (ppm)	157.12	59.48	131.92	69.60	86.53	87.30

The mixtures 1 and 3 presented a higher level of trace elements, corresponding to 157.12 and 131.92 ppm, respectively. Considering the proportion of the raw materials (Table 3.1) and the chemical composition of the mixtures, it is noted that the addition of sinter feed C results in an elevated concentration of arsenic, which causes a great impact on the total concentration of trace elements.

Mixture 2 with 59.49 ppm of trace elements, stood out due to its low levels compared to the others. This mixture showed the smallest level amongst the mixtures studied for all the trace elements evaluated, except nickel and mercury. It clarifies that a detailed knowledge of the mixture constituents can contribute to the elaborate mixtures of the low impact regarding trace elements emissions on the sintering process. The other three mixtures (4, 5, and 6) presented a very similar chemical composition.

Since the mixtures are different only in terms of sinter feed addition, these results also show the importance of this component in the mixture in terms of trace elements content. Changing only the sinter feed in the mixture, it is possible to modify to a great extent the concentration of trace elements.

3.3.3 Trace elements in the sinter

The chemical composition of the sinter, including the trace elements - As, Cd, Cu, Ni, Pb, Hg, Cl - is shown in Table 3.4. It demonstrates that the amount of trace elements in the sinter is proportional to the presence of them in the mixture, although there is not a direct relation. Sinters produced by mixtures 1 and 3 presented the highest levels of total trace elements, 141.21 ppm, and 142.67 ppm, respectively. Mixture 2, which showed the smallest levels of trace elements before burned, remained as the sinter with the less concentration of these elements reaching 56.71 ppm.

Since the concentration of these elements is too low, it was necessary to work very closely with the detection and resolution limits of the analytical methods. In this way, any small deviation caused by the methods, or even by the heterogeneous characteristics of the sinter samples and return fines, can cause an impact on the quantitative results. Then, for some cases, a negative emission factor and a recovery factor of over 100% were obtained, which does not represent a physical significance. In these cases, it was considered an emission factor of 0% and a recovery factor of 100%.

3.3.4 Trace elements distribution

With the mass obtained after each burn and the results of the respective chemical characterization, as well as the mass and the chemical characterization of the mixtures, the recovery and emission factors for each mixture were calculated using Eqts. (1) and (2). In this way it was analyzed the concentration of TEs in the flue gas before passing through the air pollution control devices. Figure 3.3 shows the results of the recovery and emission factors obtained for total trace elements in the different tested mixtures. In general, trace elements showed a greater tendency to remain in sinter, with the highest emission factor found in mixture 6 (21.43%) and mixture 1 (20.94%), chlorine being responsible for most of the emission in both mixtures. In mixture 4 all TEs was concentrated in the sinter.

Table 3.4 - Chemical analysis of sinter.

Component	M 1	M 2	M 3	M 4	M 5	M 6
Sinter product mass (kg)	49.29	48.90	49.19	51.91	50.68	52.31
Fe (%)	57.28	57.37	57.40	56.22	56.01	56.29
FeO (%)	5.54	5.22	5.58	5.10	4.87	4.73
SiO ₂ (%)	5.49	5.22	5.30	5.57	5.78	5.53
Al ₂ O ₃ (%)	1.56	1.50	1.53	1.39	1.59	1.55
P (%)	0.05	0.05	0.05	0.05	0.06	0.06
Mn (%)	0.19	0.18	0.19	0.24	0.24	0.24
CaO (%)	9.58	9.88	9.80	10.83	10.77	10.51
MgO (%)	1.56	1.58	1.64	1.31	1.23	1.24
TiO ₂ (%)	0.09	0.08	0.08	0.09	0.10	0.09
PPC (%)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
As (ppm)	66.90	10.60	69.30	11.40	10.30	9.30
Cd (ppm)	0.20	0.10	0.16	0.06	0.06	0.06
Cu (ppm)	38.00	24.10	39.10	34.10	31.90	29.00
Ni (ppm)	20.40	13.40	18.30	15.00	10.00	10.60
Pb (ppm)	15.70	8.50	15.80	9.00	8.90	9.70
Hg (ppm)	0.01	0.01	0.01	0.02	0.02	0.01
Cl (ppm)	10.00	10.00	10.00	20.00	30.00	20.00
Total trace elements (ppm)	141.21	56.71	142.67	69.58	61.18	58.68

According to Sekine *et al.* [5] and Xu *et al.* [6], trace elements can behave in three different ways in high-temperature processes. Some tend to remain in the solid-state (Cu, Cr, Mn, Co, Ni), others partially volatilize during the process and may condense before being emitted into the atmosphere (Zn, Pb, Cd, As), and some still volatilize and are emitted to the atmosphere in vapor state (Hg, F, Cl, Br). Table 3.5 presents the trace elements related to different behavior at high-temperature (non-volatile, semi-volatile, and volatile) for each mixture, aiming to have a better insight into the distribution of these elements. Since Cu and Ni, non-volatile elements, and Pb, Cd, and As, semi-volatile elements, are high (67 - 93%) in all mixtures, the trend of high concentration of trace elements in the sinter agree with results showed in Figure 3.3. Although this theoretical estimation agrees with the general trend observed in the experiments, there are divergences in terms of absolute values for each individual mixture. Mixture 5, for example, has a high volatile content, but did not present a high emission factor. This behavior occurred due to the relatively low chlorine emission factor in this mixture. The individual behavior of each element is discussed in the following topics. This divergences can be explained by the relatively low precision of the analytical methods for the concentration range of trace elements. The heterogeneity characteristic of the sinter can

also impact the results of the analysis, implying variations in results. The behavior of each trace element is individually discussed in the next topics to access in detail the behavior of these elements.

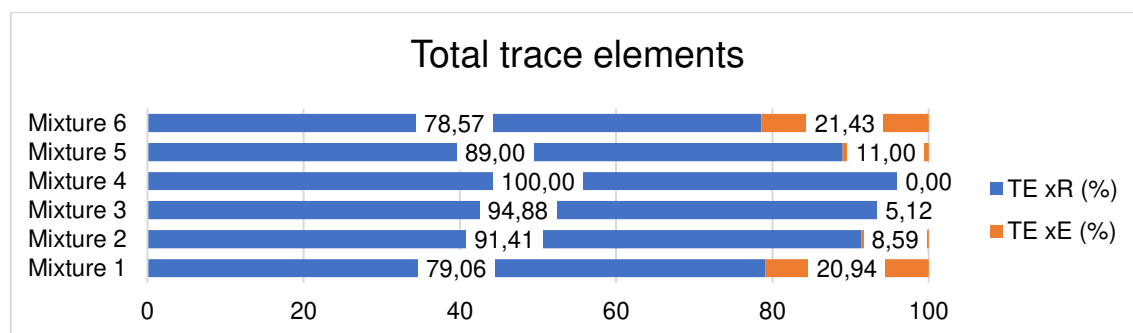


Figure 3.3 - Recovery and emission factors for total trace elements in each mixture.

Table 3.5 - Amount of trace elements classified as non-volatile, semi-volatile, and volatile in the mixtures.

Classification	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5	Mixture 6
Non-volatile (Cu, Ni)	38.62%	56.21%	37.60%	54.81%	45.95%	50.34%
Semi-volatile (As, Cd, Pb)	54.76%	28.78%	55.85%	22.84%	21.12%	24.23%
Volatile (Cl, Hg)	6.62%	15.01%	6.56%	22.35%	32.92%	25.44%

The correlation between the emission factors found for each element and the chemical composition of the sintering mixture was evaluated. Table 3.6 shows the result found. Despite the small number of samples, some statistically significant correlations could be found, especially for cadmium and lead.

Table 3.6 - Spearman's Correlation between emission factor and chemical composition of mixture.

	As		Cd		Cu		Ni		Pb		Hg		Cl	
	ρ	p-value	ρ	p-value	ρ	p-value	ρ	p-value	ρ	p-value	ρ	p-value	ρ	p-value
Fe	-0,522	0,288	0,845	0,034	-0,290	0,577	-0,145	0,784	0,778	0,069	0,314	0,544	0,314	0,544
FeO	0,464	0,354	0,778	0,069	-0,058	0,913	-0,493	0,321	0,845	0,034	-0,486	0,329	0,543	0,266
SiO ₂	0,696	0,125	-0,439	0,383	0,203	0,700	-0,348	0,499	-0,372	0,468	-0,771	0,072	-0,086	0,872
Al ₂ O ₃	0,145	0,784	0,304	0,558	0,319	0,538	0,290	0,577	0,507	0,305	0,257	0,623	0,600	0,208
P	0,754	0,084	-0,439	0,383	0,638	0,173	0,551	0,257	-0,372	0,468	-0,086	0,872	0,257	0,623
Mn	-0,609	0,200	-0,372	0,468	0,058	0,913	-0,319	0,538	-0,439	0,383	-0,200	0,704	-0,200	0,704
CaO	0,696	0,125	-0,439	0,383	0,203	0,700	-0,348	0,499	-0,372	0,468	-0,771	0,072	-0,086	0,872
MgO	-0,261	0,618	0,778	0,069	0,116	0,827	-0,203	0,700	0,845	0,034	0,029	0,957	0,714	0,111
TiO ₂	0,058	0,913	0,778	0,069	0,029	0,957	0,116	0,827	0,845	0,034	0,257	0,623	0,600	0,208
PPC	0,319	0,538	-0,845	0,034	0,029	0,957	0,058	0,913	-0,778	0,069	-0,200	0,704	-0,543	0,266
As	0,261	0,618	0,845	0,034	-0,638	0,173	-0,319	0,538	0,778	0,069	-0,029	0,957	-0,029	0,957
Cd	0,485	0,329	0,849	0,033	-0,121	0,819	-0,243	0,643	0,849	0,033	-0,239	0,648	0,478	0,338
Cu	0,464	0,354	0,778	0,069	-0,058	0,913	-0,493	0,321	0,845	0,034	-0,486	0,329	0,543	0,266
Ni	0,000	1,000	0,778	0,069	0,203	0,700	0,000	1,000	0,845	0,034	0,086	0,872	0,771	0,072
Pb	0,464	0,354	0,778	0,069	-0,058	0,913	-0,493	0,321	0,845	0,034	-0,486	0,329	0,543	0,266
Hg	0,261	0,618	-0,778	0,069	-0,116	0,827	0,203	0,700	-0,845	0,034	-0,029	0,957	-0,714	0,111
Cl	0,798	0,057	-0,237	0,651	0,360	0,483	-0,407	0,423	0,018	0,973	-0,802	0,055	0,309	0,552

Arsenic

Figure 3.4 shows the recovery and emission factors for arsenic in each mixture. In general, arsenic presented a low emission factor, where only the mixture 6 reached a value of over 20% (25.64%). Mixtures 2 and 4 presented the lowest emission factor regarding this element, which is consistent with their low contents of As. Moreover, once arsenic can volatilize as AsCl_3 [23], it can explain the highest emission factor of mixtures 3, 6, and 1 presented, since they are the richest in Cl before sintering. This hypothesis was tested using the Spearman correlation method for the initial concentration of chlorine in the mixture and the arsenic emission factor. As can be seen in Table 3.6 the result found indicates a positive monotonic correlation ($\rho = 0.798$) and a p-value of 0.057, despite the relatively small number of samples tested (high p-value).

The general tendency of arsenic to be retained in the sinter can be also explained by its combination with iron (abundant in the mixtures) to form FeAsO_4 , which is a stable phase up to 1,100 °C. Although aluminum is not in large amounts in the samples it can also interact with arsenic forming AlAsO_4 , stable up to 1,400 °C. Another possibility is the interaction with Ca forming $\text{Ca}(\text{AsO}_2)_2$ and $\text{Ca}_3(\text{AsO}_4)_2$. The latter is less likely due to the lower Ca concentration in the mixtures, the lower temperature at which these compounds are stable, and the presence of Si in the process, which has a higher affinity for Ca than As. The possibility of the formation of $\text{Cd}_3(\text{AsO}_4)_2$, which is stable between 600 and 1,200°C, is also unlikely due to the low concentration of arsenic and cadmium, resulting in low availability to react [24].

One way to avoid the emission of arsenic is through the proper choice of raw materials with a low concentration of this element. Among the sinter raw materials, the main source of arsenic is the sinter feed [19].

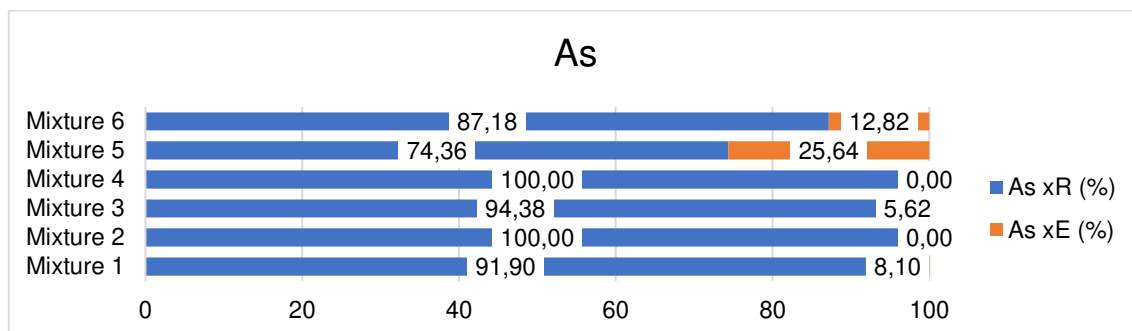


Figure 3.4 - Recovery and emission factors for arsenic in each mixture.

Cadmium

The results presented in Figure 3.5 show that the cadmium trend to concentrate on the sintered product, except for the mixture 3, which presented an emission factor of 30.96%. Although cadmium is a metal with low volatilization temperature, the main compound formed with Cd during the sintering process should be CdO, which only volatilizes at 1,559 °C [25]. In the presence of Al and Si, CdO can form CdO.Al₂O₃ and CdSiO₃, both compounds are stable at temperatures between 600 and 1,100 °C and may also be responsible for retaining cadmium in the sinter [26].

Although a correlation between the Cd emission factor and the concentration of Fe ($\rho=0.845$, $p\text{-value}=0,034$) and As ($\rho=0.845$, $p\text{-value}=0,034$) in the mixture was found by the Spearman correlation method (Table 3.6), no explanation for this correlation was found in the literature.

It is important to note, however, cadmium was identified in very lower concentrations in the mixtures and the measurements obtained were very close to the detection limits of the characterization methods, which can affect the accuracy of the analytical methods.

Among the sintering inputs, fluxes are the one with the highest concentration of Cd however, since the mass of sinter feed used is much greater than that of fluxes, the sinter feed is also the main responsible for the contribution of this element in the process [19].

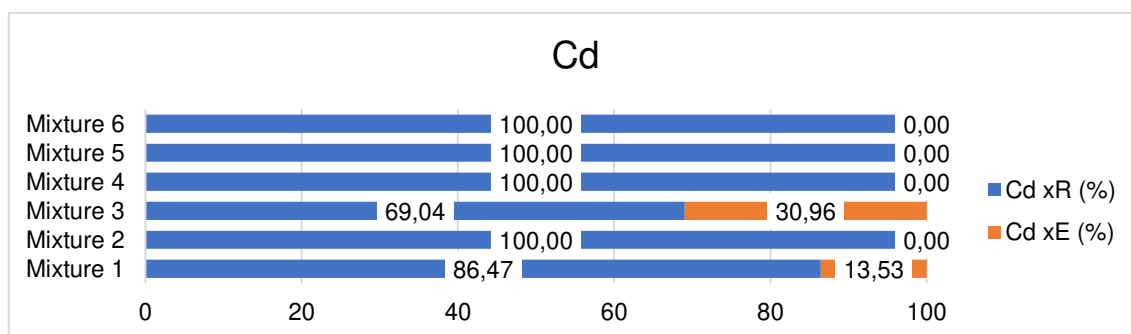


Figure 3.5 - Recovery and emission factors for cadmium in each mixture.

Copper

According to the result shown in Figure 3.6, copper presented a low emission factor, with the highest value in mixture 6 (17.38%). In general, copper compounds have a high boiling point, indicating their non-volatilization behavior in conditions of the sintering process. The main copper compound that can be formed during sintering which would have the greatest tendency to volatilize is CuCl₂, with a boiling point of 993 °C [25].

However, no correlation was found between the Cu emission factors and the composition of the 6 mixtures (Table 3.6).

The results agree with Zhang *et al.* (2013), that found very low copper concentration on fly ash and flue gas during the co-combustion of sewage sludge and coal in power plants [27]. It cannot be neglected the role of copper in catalysis in the formation of chlorinated aromatics, promoting carbon oxidation and chlorination, and being the main catalyst of these compounds [28]. According to Sun *et al.* (2016) and Zhang *et al.* (2017) the catalytic activity for the *de novo* formation (one of the main formation pathways of chlorinated aromatics) was $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} > \text{Cu}_2\text{O} > \text{Cu} > \text{CuSO}_4 > \text{CuO}$ for chlorobenzenes (CBzs), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} > \text{Cu}_2\text{O} > \text{CuO} > \text{Cu} > \text{CuSO}_4$ for polychlorinated biphenyls (PCBs) [29], and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} > \text{Cu} > \text{blank}$ for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) [11].

The main Cu concentrator among the sintering raw materials is the coke breeze, however the sinter feed is the main responsible for the input due to the greater mass used [19].

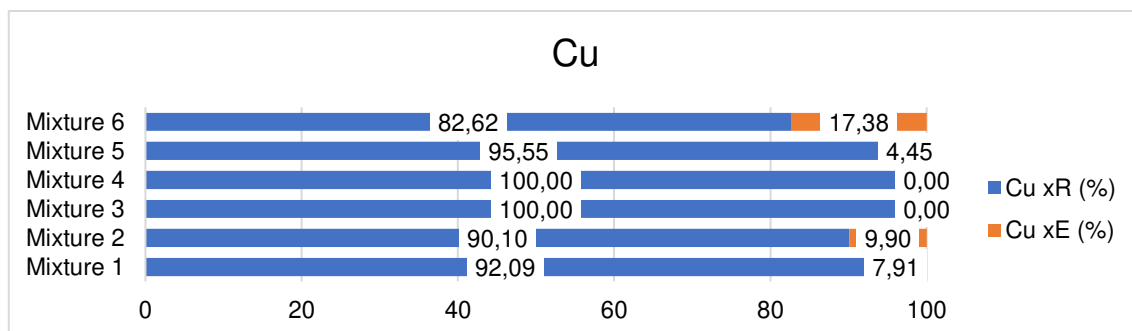


Figure 3.6 - Recovery and emission factors for copper in each mixture.

Nickel

In Figure 3.7 is shown the recovery and emission factor of Nickel, that in general stay retained in the sinter. As nickel and its main compounds have a high boiling point, so the low emission of this element is reasonable. When the nickel is emitted, it should happen by volatilization through the NiCl_2 formation, which sublimates at a temperature of 985 °C [25]. As with copper, no correlation between the nickel emission factor and the composition of the mixtures was found (Table 3.6).

That low index of nickel emission agrees with the results obtained by Zhu *et al.* (2017) that analyzes the concentration of trace elements in the soil of closed iron and steel plant

in China. The concentrations of nickel in the soil found in this study were comparable to the background concentration of this element in the earth's crust. This points to a low deposition of this element in the soil, which is considered a consequence of a low air emission [30]. Also, Zhao *et al.* (2017) studied the particulate matter emitted (PM) from different emission points of a sinter plant and found low Ni concentration on the PM from the sinter strand [31].

In a previous study it was identified that, among the main sintering inputs, coke breeze had a higher concentration of Ni, with 135.87 ppm, the other inputs had concentrations in the order of 16 ppm. Despite the large difference in concentration, iron ores still the major responsible for the absolute value of Ni that enters the process [19].

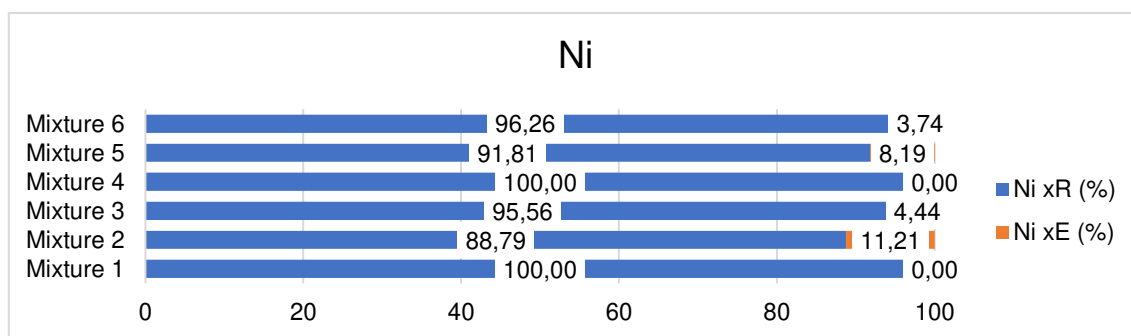


Figure 3.7 - Recovery and emission factors for nickel in each mixture.

Mercury

Different from the other elements analyzed so far, mercury has a high emission factor (more than 75% for all mixtures) as can be seen in Figure 3.8. It is reasonable since the sintering process is the first step where the iron ore is submitted to elevated temperatures (around 1,300 °C) and mercury is considered as a volatile metal, with a boiling point of 356,73 °C. It can be emitted in the form of Hg^{2+} , Hg^0 , or Hg_P . In iron ore sintering, the main form of mercury occurring in flue gas is Hg^{2+} (~ 70%), followed by Hg^0 (~ 30%) and almost none Hg_P [17, 32]. The high concentration of Hg^{2+} is due to the catalytic activity of Fe_2O_3 in the oxidation of Hg in the presence of Cl [33, 34]. As can be seen in Table 3.6, no correlation was found between the mercury emission factor and the chemical composition of the sintering mixture.

Although the air pollution control devices present high performance to remove mercury from the flue gas, (97,5 - 98,3% according to Xu *et al.* (2017)), these results deserve attention, since mercury is one of the most dangerous contaminants to the environment

and human health (toxicity, long-range transport, persistence, and bioaccumulation) [17]. Zhu *et al.* (2017) investigated heavy metal contamination in the soil of an area affected by iron and steel industry in Beijing (China). Between all heavy metals evaluated, mercury showed the largest enrichment in the soil [30]. The main responsible for the supply of mercury in the sintering process are iron ores [17, 19]

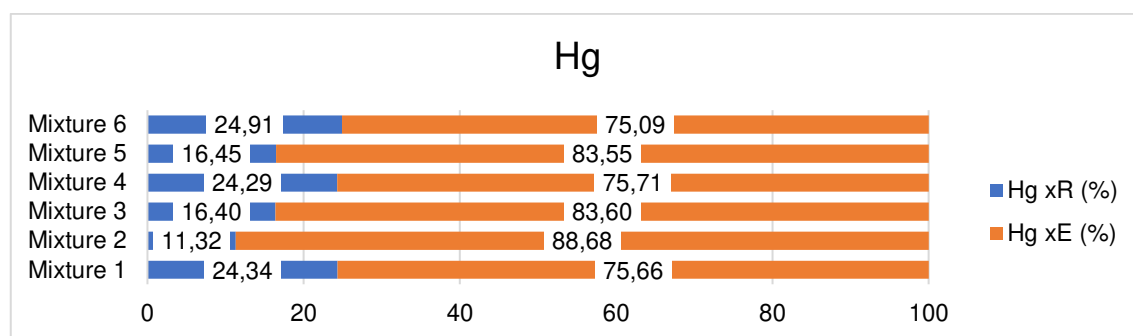


Figure 3.8 - Recovery and emission factors for mercury in each mixture.

Lead

Figure 3.9 shows lead presented low emission factor for all mixtures, except for mixture 1 (21.83%). In general, this result is consistent since the main compounds formed with lead have a high boiling point [25]. According to Remus *et al.* (2013), the emission of lead is related to the presence of chlorine in the sinter feed, with the formation of volatile compounds (PbO-PbCl_2 , PbCl_2 , and, probably, PbCl_4) [35]. Deng *et al.* (2014) found a correlation of 0.7952 between lead emission and the presence of chlorine in coal in Chinese thermoelectric plants. Considering this result in the iron ore sintering process, the presence of chlorine should favor the emission of lead [36].

In this study, on the other hand, no correlation was identified between the lead emission factor and the concentration of chlorine in the mixture. However, correlations were found with the concentrations of FeO, MgO, TiO_2 , Cd, Cu, Ni and Hg (Table 5), for which no explanation has been found in the literature. Contrary to the correlation found, according to Lin *et al.* (2010), it was expected that the increase in MgO concentration would result in a lower Pb emission factor [37].

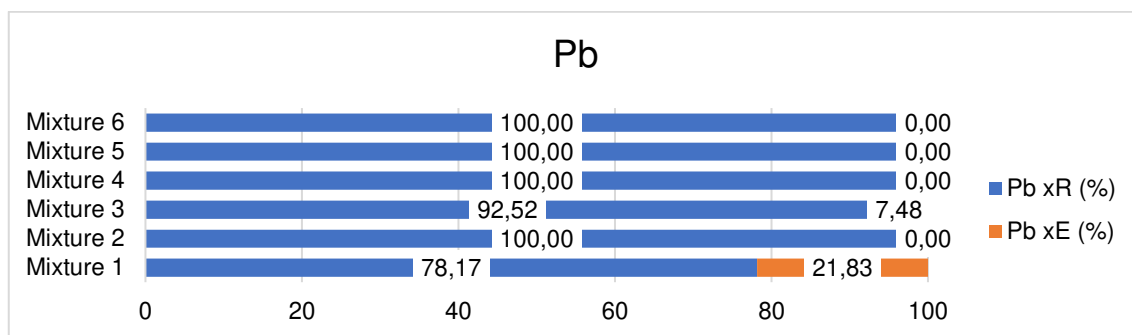


Figure 3.9 - Recovery and emission factors for lead in each mixture.

Chlorine

Chlorine presented a significant emission factor, as shown in Figure 3.10. The values of emission obtained for this element is higher than others analyzed in this work, except for mercury. The presence of chlorine has great relevance in the behavior of other trace elements, as compounds like PbCl_2 with lead, NiCl_2 , and CuCl_2 can be formed in the sintering process and to volatilize. All these compounds volatilize at temperatures below the maximum sintering temperature.

Mixtures 2, 3, 4 and 5 showed similar behavior, with emission factors varying between 13.48 and 18.50%. The mixture 6 presented an emission factor of 41.88%, and the Cl may have been emitted along with copper, since this mixture presented the highest copper emission factor. The highest chlorine emission factor found was 72.62% for mixture 1. Since this mixture also presented the highest emission factor for Pb, it is believed that the Cl emitted may be related to lead.

Moreover, the results found in this work are close to those obtained by Kawaguchi *et al.* (2002), which indicated 20 to 40% by mass of Cl does not volatilize, remaining in the sinter, and another 20 to 40% of volatile Cl stays trapped in sinter bed [38]. The presence of chlorine in the sintering process is quite relevant due to the formation of chlorinated aromatics compounds. Kawaguchi *et al.* (2002) identified a positive correlation between the concentration of Cl in the sintering mixture and the concentration of dioxins in the exhaust gas [38].

In this study, no correlation was found between the chlorine emission factor and the chemical composition of the mixtures, as can be seen in Table 3.6.

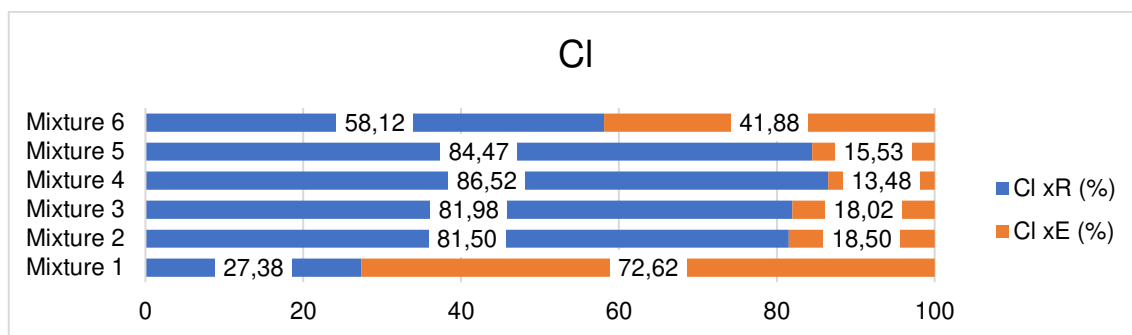


Figure 3.10 - Recovery and emission factors for Chlorine in each mixture.

3.3.5 Analysis of atmospheric emissions

For the mixtures 1, 2, and 3, samples of the flue gas were collected through CIPA equipment. This equipment collects particulate materials and trace elements presented in vapour phase. The samples were collected in the filters and the solutions were chemically characterized. When the element was not identified in the solution, the limit of detection was used as the obtained concentration value. The results of the analysis of atmospheric emissions were divided into two groups the elements in the gas phase and the elements in the solid phase (particulate material). Figure 3.11 shows that in general a higher concentration of trace elements in the solid phase, except for mercury. Results obtained for nickel also showed a significant part of this element in the gas phase.

The mixture that presented the highest emission of trace elements was the mixture 1, except concerning the copper (higher in mixture 3) and mercury (higher mixture 2). Apart from mercury, mixture 2 had a low emission of all other TEs. This can be explained observing that the concentration of each of the TEs in mixture 2 was lower than in mixtures 1 and 3, except for mercury and chlorine. Since the emission of chlorine must be related to the emissions of Pb and Cu, a lower emission of Cl was expected in this mixture.

A higher concentration of trace elements in mixture 1 seems to be the main reason to explain its higher amount of trace elements in atmospheric emission. Also, the behavior of mixtures 1 and 3 proved to be quite similar, which reveals a strong dependence between the emission and the initial concentration of trace elements in the mixture, since both have similar chemical characteristics.

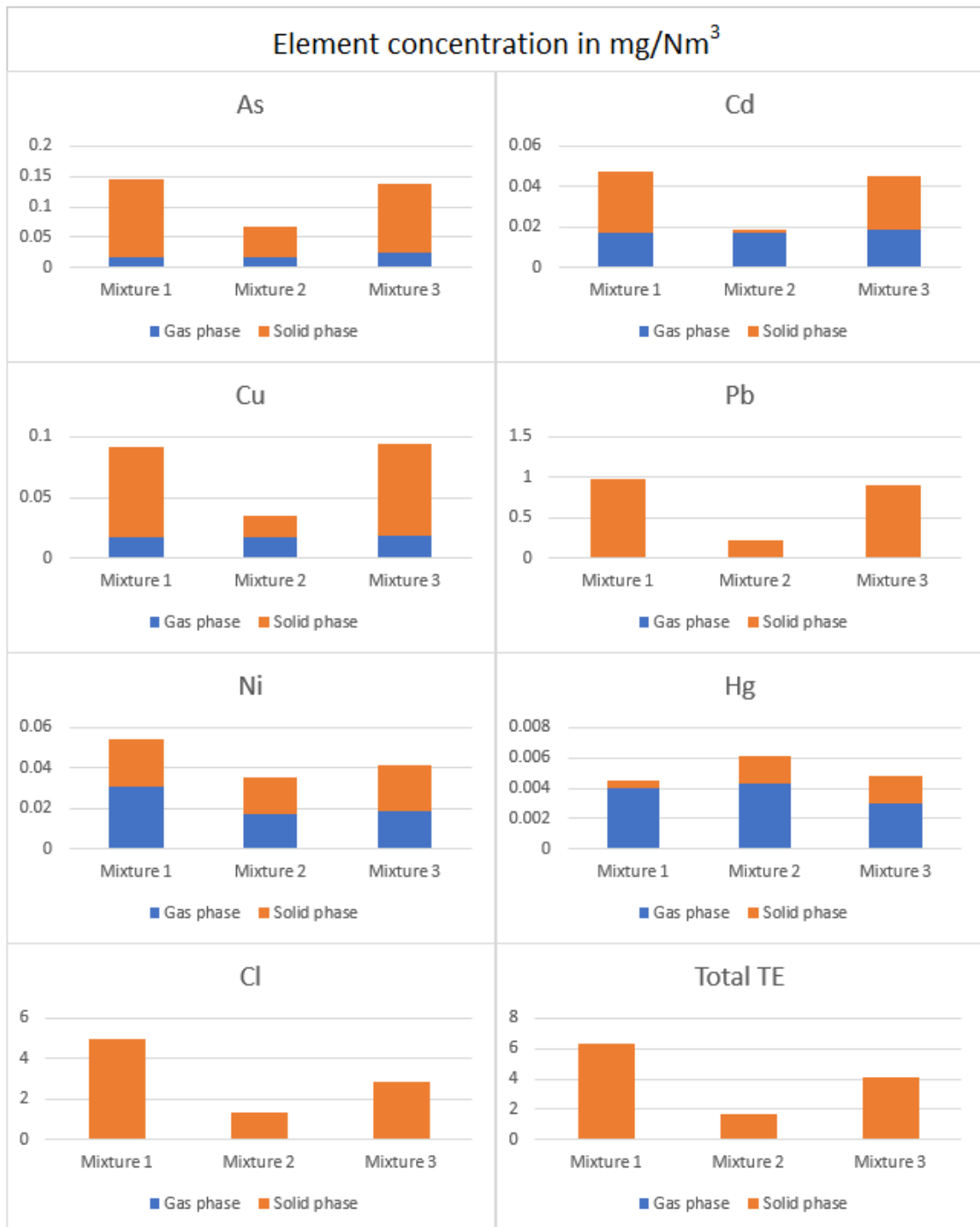


Figure 3.11 - Trace element concentration in atmospheric emission.

Chlorine was only evaluated in the solid phase and the lead showed a much higher concentration in the solid phase compared to the gaseous one, making the analysis of the total trace elements present almost total concentration in the solid phase, since the concentration found of these two elements was much higher than the others. Overall,

except for mercury, the trace elements showed a greater tendency to concentrate in the solid phases, either in the sintered product or in particulate material from emission. Among the elements that remain in the sinter, attention must be paid to the other stages of the steel production process. To avoid the emission of these elements, a evaluate the composition of the sintering mixtures is a crucial step, since this study demonstrated the direct relationship between the input of trace elements and their emission. Since most elements remain in the solid phase of emission, the use of efficient emission control methods can drastically reduce trace element emissions, especially concerning the collection of fine particulate material. Mercury is, however, the exception, due to its large emission factor and a higher concentration in the gas phase.

3.4 Conclusions

In the present work, the behavior of trace elements in the iron ore sintering was evaluated through a sinter pot test and different sintering mixtures. As and Cu were identified as the major trace elements in the mixtures before sintering, while Hg and Cd were detected in low concentration. After sintering, the trace elements evaluated in this work showed a clear trend to remain in the sinter, except for Hg. The emission of trace elements was higher for mixtures with high trace elements content, which reveals the possibility to control the emission of these elements in the sintering process by adjusting the composition of the mixture. Moreover, as these elements were also majorly found in the solid particulates of the emission, the equipment that controls the particulates emission must have high efficiency. Some correlations between components of sintering mixture and trace elements emission have also been identified. The arsenic and lead emission increased in the presence of chlorine in the mixture, while the cadmium emission had a positive correlation with arsenic and iron content in the mixture. To improve the understanding of the behavior of trace elements in the sintering process, continuous efforts toward to enlarge the database is necessary.

3.5 Acknowledgment

The authors express gratitude to CAPES-PROEX, CNPq and FAPEMIG for accomplishment and support of this work.

3.6 References

- [1] C.O.T.E.U. European Parliament, Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, in: C.O.T.E.U. European Parliament (Ed.) Official Journal of the European Union, 2008, pp. 169 - 212.
- [2] M.o.E.P.o. China, Emission standard of air pollutants for sintering and pelletizing of iron and steel industry, in: M.o.E.P.o. China (Ed.) GB 28662-2012, China Environmental Science Press, 2012, p. 5.
- [3] Z. Ji, X. Fan, M. Gan, X. Chen, Q. Li, Y. Tian, X. He, Y. Zhou, T. Jiang, Influence Factors on PM_{2.5} and PM₁₀ Emissions in Iron Ore Sintering Process, *ISIJ International* 56(9) (2016) 1580-1587.
- [4] A. Przybysz, A. Sæbø, H.M. Hanslin, S.W. Gawroński, Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time, *Science of The Total Environment* 481 (2014) 360-369.
- [5] Y. Sekine, K. Sakajiri, E. Kikuchi, M. Matsukata, Release behavior of trace elements from coal during high-temperature processing, *Powder Technology* 180(1) (2008) 210-215.
- [6] M. Xu, R. Yan, C. Zheng, Y. Qiao, J. Han, C. Sheng, Status of trace element emission in a coal combustion process: a review, *Fuel Processing Technology* 85(2) (2004) 215-237.
- [7] C. Boente, N. Matanzas, N. García-González, E. Rodríguez-Valdés, J.R. Gallego, Trace elements of concern affecting urban agriculture in industrialized areas: A multivariate approach, *Chemosphere* 183 (2017) 546-556.
- [8] C.L. Senior, Development of a mechanistic model for prediction of emission of trace elements from coal-fired power plants, *Fuel Processing Technology* 63(2) (2000) 75-77.
- [9] S. Zhao, Y. Duan, C. Li, Y. Li, C. Chen, M. Liu, J. Lu, Partitioning and Emission of Hazardous Trace Elements in a 100 MW Coal-Fired Power Plant Equipped with Selective Catalytic Reduction, Electrostatic Precipitator, and Wet Flue Gas Desulfurization, *Energy & Fuels* 31(11) (2017) 12383-12389.
- [10] H. Tian, K. Liu, J. Zhou, L. Lu, J. Hao, P. Qiu, J. Gao, C. Zhu, K. Wang, S. Hua, Atmospheric Emission Inventory of Hazardous Trace Elements from China's Coal-Fired

Power Plants—Temporal Trends and Spatial Variation Characteristics, *Environmental Science & Technology* 48(6) (2014) 3575-3582.

[11] Y. Zhang, L. Liu, Y. Sun, R. Zhu, X. Gao, J. Yang, Z. Han, H. Wang, Formation of persistent chlorinated aromatic compounds in simulated and real fly ash from iron ore sintering, *Journal of Material Cycles and Waste Management* 19(4) (2017) 1437-1445.

[12] G.C. Abreu, J.A.d. Carvalho, B.E.C.d. Silva, R.H. Pedrini, Operational and environmental assessment on the use of charcoal in iron ore sinter production, *Journal of Cleaner Production* 101 (2015) 387-394.

[13] G.M. Olmez, F.B. Dilek, T. Karanfil, U. Yetis, The environmental impacts of iron and steel industry: a life cycle assessment study, *Journal of Cleaner Production* 130 (2016) 195-201.

[14] Y. Chen, Z. Guo, Z. Wang, Influence of CeO₂ on NO_x emission during iron ore sintering, *Fuel Processing Technology* 90(7) (2009) 933-938.

[15] N. Menad, H. Tayibi, F.G. Carcedo, A. Hernández, Minimization methods for emissions generated from sinter strands: a review, *Journal of Cleaner Production* 14(8) (2006) 740-747.

[16] J.-H. Tsai, K.-H. Lin, C.-Y. Chen, J.-Y. Ding, C.-G. Choa, H.-L. Chiang, Chemical constituents in particulate emissions from an integrated iron and steel facility, *Journal of Hazardous Materials* 147(1) (2007) 111-119.

[17] W. Xu, M. Shao, Y. Yang, R. Liu, Y. Wu, T. Zhu, Mercury emission from sintering process in the iron and steel industry of China, *Fuel Processing Technology* 159 (2017) 340-344.

[18] F. Wang, S. Wang, L. Zhang, H. Yang, W. Gao, Q. Wu, J. Hao, Mercury mass flow in iron and steel production process and its implications for mercury emission control, *Journal of Environmental Sciences* 43 (2016) 293-301.

[19] L.L. Lau, L.F.A. de Castro, F.d.C. Dutra, M.V. Cantarino, Characterization and mass balance of trace elements in an iron ore sinter plant, *Journal of Materials Research and Technology* 5(2) (2016) 144-151.

[20] U.S. EPA, STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES (CONTINUED), in: U.S. EPA (Ed.) Title 40, Electronic Code of Federal Regulations.

- [21] U.S. EPA, Compendium Method IO-3.3 - DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY, 1999.
- [22] D. Fernández-González, I. Ruiz-Bustanza, J. Mochón, C. González-Gasca, L.F. Verdeja, Iron Ore Sintering: Raw Materials and Granulation, *Mineral Processing & Extractive Metallurgy Review* 38(1) (2017) 36-46.
- [23] S. Zhao, Y. Duan, Y. Li, M. Liu, J. Lu, Y. Ding, X. Gu, J. Tao, M. Du, Emission characteristic and transformation mechanism of hazardous trace elements in a coal-fired power plant, *Fuel* 214 (2018) 597-606.
- [24] M.L. Contreras, J.M. Arostegui, L. Armesto, Arsenic interactions during co-combustion processes based on thermodynamic equilibrium calculations, *Fuel* 88(3) (2009) 539-546.
- [25] C.R. Hammond, The Elements, in: W.M. Haynes (Ed.), *CRC Handbook of Chemistry and Physics*, CRC Press 2016.
- [26] Z. Zhu, Y. Huang, J. Zha, M. Yu, X. Liu, H. Li, X. Zhu, Emission and Retention of Cadmium during the Combustion of Contaminated Biomass with Mineral Additives, *Energy & Fuels* 33(12) (2019) 12508-12517.
- [27] G. Zhang, J. Hai, M. Ren, S. Zhang, J. Cheng, Z. Yang, Emission, Mass Balance, and Distribution Characteristics of PCDD/Fs and Heavy Metals during Cocombustion of Sewage Sludge and Coal in Power Plants, *Environmental Science & Technology* 47(4) (2013) 2123-2130.
- [28] L. Liu, W. Li, Z. Xiong, D. Xia, C. Yang, W. Wang, Y. Sun, Synergistic effect of iron and copper oxides on the formation of persistent chlorinated aromatics in iron ore sintering based on in situ XPS analysis, *Journal of Hazardous Materials* 366 (2019) 202-209.
- [29] Y. Sun, L. Liu, X. Fu, T. Zhu, A. Buekens, X. Yang, Q. Wang, Mechanism of unintentionally produced persistent organic pollutant formation in iron ore sintering, *Journal of Hazardous Materials* 306 (2016) 41-49.
- [30] G. Zhu, Q. Guo, H. Xiao, T. Chen, J. Yang, Multivariate statistical and lead isotopic analyses approach to identify heavy metal sources in topsoil from the industrial zone of Beijing Capital Iron and Steel Factory, *Environmental Science and Pollution Research* 24(17) (2017) 14877-14888.

- [31] L. Zhao, W. Sun, X. Li, Z. Ye, J. Huang, G. Zhang, J. Cai, Assessment of particulate emissions from a sinter plant in steelmaking works in China, *Environmental Monitoring and Assessment* 189(8) (2017) 368.
- [32] Q. Wu, W. Gao, S. Wang, J. Hao, Updated atmospheric speciated mercury emissions from iron and steel production in China during 2000–2015, *Atmos. Chem. Phys.* 17(17) (2017) 10423-10433.
- [33] G.E. Dunham, R.A. DeWall, C.L. Senior, Fixed-bed studies of the interactions between mercury and coal combustion fly ash, *Fuel Processing Technology* 82(2) (2003) 197-213.
- [34] S. Ghorishi, C. Lee, W. Jozewicz, J. Kilgroe, Effects of Fly Ash Transition Metal Content and Flue Gas HCl/SO₂ Ratio on Mercury Speciation in Waste Combustion, *Environmental Engineering Science - ENVIRON ENG SCI* 22 (2005) 221-231.
- [35] R. Remus, M. Aguado Monsonet, S. Roudier, L. Delgado Sancho, Best Available Techniques (BAT) Reference Document for Iron and Steel Production, Luxembourg, 2012, p. 597.
- [36] S. Deng, Y. Shi, Y. Liu, C. Zhang, X. Wang, Q. Cao, S. Li, F. Zhang, Emission characteristics of Cd, Pb and Mn from coal combustion: Field study at coal-fired power plants in China, *Fuel Processing Technology* 126 (2014) 469-475.
- [37] C.-L. Lin, S.-H. Chang, T.-H. Peng, Investigation on the Emission of Heavy Metals in Fluidized-Bed Incineration during the Agglomeration/Defluidization Process, *Energy & Fuels* 24(5) (2010) 2910-2917.
- [38] T. Kawaguchi, M. Matsumura, Y. Hosotani, E. Kasai, Behavior of Trace Chlorine in Sintering Bed and Its Effect on Dioxins Concentration in Exhaust Gas of Iron Ore Sintering, *Journal Of The Iron And Steel Institute Of Japan* 88(2) (2002) 59-65.

Capítulo 4. Considerações finais

4.1 Conclusões gerais

No presente trabalho, o comportamento de sete elementos-traço (arsênio, cádmio, chumbo, cloro, cobre, mercúrio e níquel) no processo de sinterização de minério de ferro foi avaliado. No artigo apresentado no Capítulo 2, foi elaborada uma extensa revisão da literatura acerca do comportamento desses elementos na sinterização, em processos correlatos e a eficiência das diversas técnicas de controle das emissões atmosféricas. Já no artigo do Capítulo 3 foi efetuado um balanço de massa desses elementos a partir de ensaios de sinterização em escala piloto, conjugado com uma análise dos gases de emissão.

Durante a elaboração do artigo do Capítulo 2 foi possível identificar que, embora já bastante estudado para alguns processos, como termelétricas a carvão e pirólise de resíduos sólidos urbanos, ainda são escassos os estudos acerca do comportamento dos elementos-traço no processo de sinterização. Além disso, alguns elementos apresentam um volume maior de estudos e estudos mais aprofundados, como é o caso, por exemplo, do arsênio e do mercúrio.

A partição dos elementos-traço no processo de sinterização de minério de ferro mostrou-se fortemente dependente das características químicas e físicas das matérias-primas e insumos, das condições do processo e dos meios de controle das emissões utilizados. Já o comportamento de cada elemento-traço avaliado depende da temperatura de volatilização, solubilidade e reatividade do elemento e dos compostos formados.

O primeiro aspecto a ser abordado quando se trata da emissão dos elementos-traço na sinterização é a composição da mistura de sinterização. Pode-se dizer que, controlar a entrada de um elemento no processo através da escolha adequada das matérias-primas é a maneira mais direta de reduzir sua emissão.

Em estudo anterior foi feita uma extensa caracterização de insumos da sinterização, a fim de se entender a participação de cada um deles no aporte dos elementos-traço. Esse estudo é apresentado no Anexo A deste trabalho.

De acordo com os resultados encontrados, os insumos da sinterização com maior concentração de elementos-traço foram os resíduos siderúrgicos. Do ponto de vista quantitativo, o principal responsável pela entrada de elementos-traço no processo é o minério ferro, uma vez que aproximadamente 60% da mistura de sinterização é

composta por esse insumo. Evidenciou-se também uma grande variedade na concentração de elementos-traço entre diversos minérios de ferro caracterizados. Essa variação ocorre em função da geologia de origem, granulometria e beneficiamento do minério, sendo que os minérios brasileiros apresentaram, de maneira geral, concentrações de elementos-traço inferiores à de minérios de outras origens estudadas (África do Sul, Austrália, Índia, China e Canadá). Embora esses resultados reforcem a ideia de que, ajustar a composição da mistura com as matérias-primas que possuem baixa concentração de elementos-traço como uma boa alternativa, nem sempre é possível modificar as matérias-primas em razão das necessidades do processo, bem como da disponibilidade e custo da matéria-prima.

Dessa forma, o próximo passo para controlar as emissões dos elementos-traço está associado às características de operação da sinterização. De maneira geral, uma elevada temperatura de queima, uma atmosfera mais oxidante e a presença de cloretos e sulfetos na mistura favorecem a volatilização e, conseqüentemente, a emissão desses elementos. A presença de sulfetos na mistura está associada principalmente ao combustível, em especial o coque, sendo possível ajustá-la com a escolha adequada dessa matéria-prima. Por outro lado, identificou-se concentrações semelhantes de cloro em diversas matérias-primas, dessa forma o sinter feed aparece como principal alternativa para o controle do aporte deste elemento, devido à sua elevada proporção na mistura de sinterização.

De acordo com a literatura, dentre os elementos estudados o cobre e o níquel tendem a permanecer no estado sólido durante o processo, ficando majoritariamente retido no sinter produto. Em ambos os casos, a presença de cloro pode impactar na sua volatilização, provocando um aumento na sua emissão. Além disso, o cobre possui grande relevância devido ao seu papel como catalizador na formação de poluentes orgânicos.

O arsênio, o cádmio e chumbo apresentaram um comportamento intermediário. Os três elementos obtiveram um fator de emissão sutilmente maior do que o cobre e o níquel. Esse comportamento foi identificado tanto experimentalmente quanto através da revisão dos estudos da literatura, que indicam que esses elementos e alguns de seus compostos apresentam uma temperatura de volatilização inferior à temperatura máxima da sinterização, volatizando parcialmente durante a queima e podendo condensar novamente antes de serem emitidos para a atmosfera. Durante o balanço de massa obteve-se uma correlação positiva entre a emissão de arsênio e a presença de cloro na

mistura. O cádmio apesar de apresentar uma temperatura de volatilização relativamente baixa, encontra-se na mistura de sinterização majoritariamente como óxido, o qual possui uma temperatura de volatilização superior à temperatura máxima atingida no processo de sinterização, resultando na volatilização parcial deste elemento. Já o chumbo, de acordo com a literatura, deveria ser emitido quando na presença de cloro, no entanto, não foi comprovado esse fato através do estudo experimental.

Por fim, o cloro e o mercúrio apresentaram maior tendência a se concentrar nas emissões quando comparados aos demais elementos avaliados. Esse fato era esperado devido à baixa temperatura de volatilização desses dois elementos. A análise do gás permitiu comprovar tal ocorrência para o mercúrio. Por outro lado, o cloro não foi caracterizado na amostra gasosa, apenas no particulado coletado, inviabilizando esse tipo de análise. Enquanto o mercúrio é emitido, majoritariamente, na forma de Hg^{2+} , a emissão do cloro associa-se à emissão de outros elementos, como por exemplo Pb e Cu.

Caso a emissão dos elementos-traço não possa ser controlada pela escolha adequada dos insumos ou pelo ajuste dos parâmetros do processo, o uso dos dispositivos de controle de emissões atmosféricas pode ter uma contribuição relevante para o abatimento desses elementos. Embora o uso de equipamentos específicos para redução das emissões de elementos-traço não seja usual, dispositivos utilizados para controle de outros poluentes apresentam resultados significativos na retenção de elementos-traço.

Diversas alternativas de equipamentos de controle de emissões atmosféricas em escala industrial podem ser usadas isoladamente ou em combinação. A maior parte dos elementos-traço retidos nesses equipamentos estão associados aos materiais particulados, porém elementos voláteis ou semivoláteis, como mercúrio, cloro, arsênio, cádmio e chumbo, podem ser emitidos na forma gasosa ou concentrados nas partículas mais finas, dificultando a sua retenção. Os equipamentos que apresentam maior eficiência na retenção dos elementos-traço associados aos materiais particulados são os ESP e os FF, sendo que equipamentos mais modernos apresentam melhor eficiência na retenção de partículas mais finas e, conseqüentemente, de elementos-traço. A associação destes equipamentos com SCR e WFGD é apresentada como a alternativa com maior eficiência na remoção dos elementos-traço totais, atuando tanto nos particulados quanto na fase gasosa.

Outras alternativas têm sido estudadas como método de controle da emissão desses elementos. Uma possibilidade é o resfriamento do gás, forçando a condensação desses elementos e os coletando como particulados. Porém a necessidade de reaquecer o gás para emití-lo nas chaminés faz com que esse processo não seja atrativo economicamente. Tem sido também explorada a utilização de adsorventes para a captura desses elementos. Nesse sentido, o uso de carvão ativado tem apresentado resultados satisfatórios na adsorção de mercúrio e arsênio. Outros adsorventes que têm sido testados e apresentado resultados promissores são aqueles à base de sílica, cálcio e paládio

De maneira geral, o comportamento dos elementos-traço no processo de sinterização é bastante complexo. A baixa concentração desses elementos torna difícil a completa compreensão dos fenômenos associados à sua partição, em parte devido à limitação dos métodos de caracterização para concentrações muito baixas. Apesar de tais dificuldades, o uso de técnicas como o balanço de massa e análise de gás, embasados pelo conhecimento difundido na literatura, permitiu propor comportamentos para cada elemento e, desta forma, oferecer subsídios para ações com o intuito de controlar a emissão desses elementos.

4.2 Contribuições originais ao conhecimento

As principais contribuições do presente trabalho para o conhecimento acerca do comportamento dos elementos-traço foram:

1. Revisão bibliográfica que contextualiza de forma original os dados da literatura referentes ao comportamento dos elementos-traço com as características do processo de sinterização e seus sistemas de controle de emissões;
2. Resultados de experimentos realizados em escala piloto com medições dos elementos-traço (arsênio, cádmio, chumbo, cloro, cobre, mercúrio e níquel) e determinação das suas partições entre sinter produto e emissões;
3. Identificação do comportamento de partição dos elementos-traço relacionado a presença de cloretos e sulfetos;
4. Embasamento para a tomada de decisões acerca das técnicas de controle das emissões a serem utilizadas para cada elemento-traço.

4.3 Sugestões para trabalhos futuros

São sugeridos os seguintes temas para trabalhos futuros:

1. Efetuar balanço de massa e análise de gás em planta de sinterização de minério de ferro de escala industrial, avaliando a concentração de elementos-traço no sinter e nos resíduos coletados por cada dispositivo de controle de emissões atmosféricas;
2. Identificar como os principais elementos-traço estão associados ao minério e qual a influência da mineralogia nas partições destes elementos;
3. Avaliar as possíveis relações entre as propriedades físicas dos insumos (granulometria, porosidade, etc) com a liberação dos elementos-traço durante o processo de sinterização;
4. Estudar o aporte, comportamento e emissões dos elementos-traço no alto-forno;
5. Desenvolvimento de modelo matemático capaz de prever as emissões dos elementos-traço.

APÊNDICE A – Resultados do balanço de massa

Tabela A.1 – Resultados do balanço de massa.

	Mistura	Massa (kg)	Concentração de ET (ppm)							Massa de ET (g)						
			As	Cd	Cu	Ni	Pb	Hg	Cl	As	Cd	Cu	Ni	Pb	Hg	Cl
Entrada	Mistura 1	60,00	59,8	0,19	33,9	16,7	16,5	0,027	30	3,588	0,011	2,034	1,002	0,990	0,00162	1,8
	Mistura 2	60,00	8,4	0,04	21,8	12,3	6,9	0,036	10	0,504	0,002	1,308	0,738	0,414	0,00216	0,6
	Mistura 3	60,00	60,2	0,19	31,8	15,7	14	0,03	10	3,612	0,011	1,908	0,942	0,840	0,0018	0,6
	Mistura 4	60,00	9,8	0,04	24,5	8,2	7	0,057	20	0,588	0,002	1,470	0,492	0,420	0,00342	1,2
	Mistura 5	60,00	11,7	0,05	28,2	9,2	7,3	0,077	30	0,702	0,003	1,692	0,552	0,438	0,00462	1,8
	Mistura 6	60,00	9,3	0,05	30,6	9,6	7,7	0,049	30	0,558	0,003	1,836	0,576	0,462	0,00294	1,8
Saída	Mistura 1	49,29	66,9	0,2	38,0	20,4	15,7	0,008	10	3,298	0,010	1,873	1,006	0,774	0,00039	0,5
	Mistura 2	48,90	10,6	0,1	24,1	13,4	8,5	0,005	10	0,518	0,005	1,178	0,655	0,416	0,00024	0,5
	Mistura 3	49,19	69,3	0,2	39,1	18,3	15,8	0,006	10	3,409	0,008	1,923	0,900	0,777	0,00030	0,5
	Mistura 4	51,91	11,4	0,1	34,1	15,0	9,0	0,016	20	0,592	0,003	1,770	0,779	0,467	0,00083	1,0
	Mistura 5	50,68	10,3	0,1	31,9	10,0	8,9	0,015	30	0,522	0,003	1,617	0,507	0,451	0,00076	1,5
	Mistura 6	52,31	9,3	0,1	29,0	10,6	9,7	0,014	20	0,486	0,003	1,517	0,554	0,507	0,00073	1,0
Fatores de recuperação e emissão	Mistura	xR (%)*							xE (%)*							
		As	Cd	Cu	Ni	Pb	Hg	Cl	As	Cd	Cu	Ni	Pb	Hg	Cl	
	Mistura 1	91,90	86,47	92,09	100,00	78,17	24,34	27,38	8,10	13,53	7,91	0,00	21,83	75,66	72,62	
	Mistura 2	100,00	100,00	90,10	88,79	100,00	11,32	81,50	0,00	0,00	9,90	11,21	0,00	88,68	18,50	
	Mistura 3	94,38	69,04	100,00	95,56	92,52	16,40	81,98	5,62	30,96	0,00	4,44	7,48	83,60	18,02	
	Mistura 4	100,00	100,00	100,00	100,00	100,00	24,29	86,52	0,00	0,00	0,00	0,00	0,00	75,71	13,48	
Mistura 5	74,36	100,00	95,55	91,81	100,00	16,45	84,47	25,64	0,00	4,45	8,19	0,00	83,55	15,53		
Mistura 6	87,18	100,00	82,62	96,26	100,00	24,91	58,12	12,82	0,00	17,38	3,74	0,00	75,09	41,88		

*Em alguns casos o fator de recuperação calculado foi superior a 100%. Nesses casos foi considerado que todo o elemento foi recuperado, ou seja, xR = 100% e xE = 0,00 %

APÊNDICE B – Resultados da análise de gás

Tabela B.1 – Resultados da análise de gás.

Fase	ET	Concentração de elementos-traço (mg/Nm ³)											
		Mistura 1				Mistura 2				Mistura 3			
		Queima 1	Queima 2	Queima 3	Média	Queima 1	Queima 2	Queima 3	Média	Queima 1	Queima 2	Queima 3	Média
Gasosa	As	<0,017	<0,016	<0,017	<0,017	<0,019	<0,017	<0,014	<0,017	0,022	0,021	0,032	0,025
	Cd	<0,017	<0,016	<0,017	<0,017	<0,019	<0,017	<0,014	<0,017	<0,0188	<0,0192	<0,0189	<0,0190
	Cu	<0,017	<0,016	<0,017	<0,017	<0,019	<0,017	<0,014	<0,017	<0,0188	<0,0192	<0,0189	<0,0190
	Ni	<0,017	<0,016	<0,017	<0,017	<0,019	<0,018	0,045	0,031	<0,0188	<0,0192	<0,0189	<0,0190
	Pb	<0,017	<0,016	<0,017	<0,017	<0,019	<0,017	<0,014	<0,017	<0,0188	<0,0192	<0,0189	<0,0190
	Hg	0,0047	0,0034	0,0049	0,0043	0,004	0,005	0,005	0,005	0,0038	0,0035	0,0018	0,0030
Sólida	As	0,05769	0,04269	0,05198	0,05079	0,1326	0,1509	0,1043	0,12927	0,106	0,132	0,103	0,11367
	Cd	0,00166	ND	0,00219	0,00193	0,0261	0,0363	0,0287	0,03037	0,0254	0,0301	0,0231	0,0262
	Cu	0,02026	0,01104	0,02217	0,01782	0,0649	0,0838	0,0767	0,07513	0,0598	0,0976	0,0686	0,07533
	Ni	0,01663	0,01635	0,0219	0,01829	0,0177	0,028	0,018	0,02123	0,0136	0,033	0,0204	0,02233
	Pb	0,1702	0,26458	0,17039	0,20172	0,8621	1,0623	0,9782	0,96753	0,7914	1,1365	0,7455	0,89113
	Hg	0,0019	ND	0,0018	0,00185	ND	0,00049	ND	0,00049	ND	ND	0,0018	0,0018
	Cl	1,47	0,022	2,489	1,327	2,914	5,778	6,269	4,987	0,877	3,457	4,128	2,82067

ANEXO A – Characterization and mass balance of trace elements in an iron ore sinter plant

J MATER RES TECHNOL. 2016;5(2):144-151



Available online at www.sciencedirect.com

jmr&t
Journal of Materials Research and Technology
www.jmrt.com.br



Original Article

Characterization and mass balance of trace elements in an iron ore sinter plant



Lucas Ladeira Lau^{a,*}, Luiz Fernando Andrade de Castro^a, Flavio de Castro Dutra^b,
Marcos Vinícius Cantarino^b

^a Post-Graduate Program in Metallurgical Engineering, Materials and Mining, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil

^b Centro de Tecnologia de Ferrosos, Vale, Nova Lima, MG, Brazil

ARTICLE INFO

Article history:

Received 26 September 2015

Accepted 27 October 2015

Available online 1 February 2016

Keywords:

Sintering

Trace elements

Characterization

Mass balance

Emissions

ABSTRACT

Environmental legislation is becoming more restrictive in several industrial sectors, especially in the steel industry, which is well known for its large pollution potential. With the recent growth of interest in effects of trace elements on the environment and health, the inclusion of emission limits on these elements in this legislation has become increasingly popular. This article aims to describe the partitioning of trace elements between the products (sinter) and plant emissions in an iron ore sinter plant, aiming to better understand the behavior of these elements in the sintering process to eventually support interventions to modify these partitions. Chemical characterization of several sintering inputs was initially performed, revealing that the steel-making residues contained large concentrations of trace elements, whereas low concentrations were observed in the flux. Based on the trace element concentrations, we analyzed the injection of trace elements in a sintering pilot using a sintering mixture. Mass balance was then used to determine the theoretical partitioning of trace elements in the sinter and emissions; cadmium, nickel, lead, mercury, and copper exhibited greater tendencies to concentrate in atmospheric emissions.

© 2015 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. All rights reserved.

1. Introduction

The steel industry is known for its large pollution potential. With the new stricter environmental legislation, new studies have been conducted, and more precise emission controls have been implemented. The European Union, which has a very strict environmental legislation when compared to the

rest of the world, has, for the steel industry, restrictive limits for a large number of pollutants; in addition, the legislation defines specific values for each process, operational condition, and abatement technology. Moreover, the limits for the concentration of SO₂, NO₂ and PM₁₀ are more restrictive when compared to other countries [1]. The European legislation is also noteworthy for its efforts to introduce restrictions on the concentration of PM_{2.5} in the air and for including restrictive

* Corresponding author.

E-mail: lucaslau@gmail.com (L. L. Lau).
<http://dx.doi.org/10.1016/j.jmrt.2015.10.007>

2238-7854/© 2015 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. All rights reserved.

limits for some trace elements such as lead, arsenic, cadmium and nickel [1-3].

Mirroring the European Union, the remainder of the world has adopted new environmental laws and revised current ones, generating greater environmental pressure on the mining and metallurgy industry. This practice is evident in China, which has shown signs of progress in their legislation [4]. For example, recently, the limits of Chinese emission were reduced drastically, from 150mg/Nm³ to 50mg/Nm³ in the case of particulate matter, and 2000mg/Nm³ to 200 mg/Nm³ for SOx [5].

With the recent growth of interest in the effect of trace elements on the environment and health, the inclusion of certain emission limits for these elements has been increasingly observed as laws have evolved. From the viewpoint of environmental impacts, 14 elements are considered to have potentially higher impact: arsenic, cadmium, chlorine, copper, chromium, manganese, mercury, lead, nickel, vanadium, zinc, polonium, uranium, and thorium [6]. These elements are associated with the main inputs of the steel industry, and, when present in the sinter, can affect (positively or negatively) the steel chain and final product [7].

The gaseous emissions from a sinter plant significantly contribute toward the total emissions of an integrated steel mill and are considered the leading emitter of particulates [8]. Sintering accounts for approximately 45% of all particulate emissions of an integrated steel plant and emerges as the leading emitter of trace elements [9]. The input of these elements in the process occurs through the raw materials, which consist of iron ore, fuels, fluxes, and steel-making residues.

In this paper, for the first time, chemical characterization of trace elements in various sintering inputs was performed, and the intake of these elements in a sintering pilot was then analyzed using a sintering mixture. The mass balance was then considered to determine the theoretical partitioning of trace elements in the products (sinter) and emissions. Therefore, this study describes the partitioning of trace elements between the products and plant emissions, with the aim of better understanding the behavior of these elements in the sintering process to eventually support interventions to modify these partitions.

2. Methods

2.1. Chemical characterization of inputs

In the sintering process, a mixture of raw materials composed of fine ore (sinter feed), solid fuel (coke), flux, returned fines, and steel-making residues is arranged on a conveyor belt and then heated to temperatures close to 1300°C to achieve reductive-oxidizing semifusion. The product of this process is a mass called sinter [10], which is then crushed; its particle size is adjusted through screening to meet the requirements of the next stages of steel production, and the thin material is reused in the process.

In this study, chemical characterization of various sintering inputs was conducted. These inputs were divided into 11 categories (sinter feed, pellet feed, lump, concentrate, pellet, pellet fine, lump and sinter fines, returned fines, fuel, fluxes,

Table 1 – Description of sintering input samples characterized.

Type of sample	Origin	Number of samples
Sinter feed	Brazil	17
	South Africa	2
	Australia	13
	China	2
	India	2
Pellet feed	Brazil	5
	Canada	1
	China	17
Lump	Brazil	6
Concentrate	China	9
Pellet	Brazil	1
Pellet fines	Brazil	1
Lump and sinter fines	Brazil	1
Returned fines	Brazil	1
Fuels	Brazil	2
	China	1
Fluxes	Brazil	2
	China	5
Steel-making residues	Brazil	9
Total		97

and steel-making residues), and the average concentrations of each trace element in each of these categories were evaluated. We then studied the concentration distribution of each trace element in each of these categories using column charts. Table 1 provides a description of the samples.

It is not possible to include further details of the chemical analysis method since this work was conducted by two different global laboratories, ALS and SGS Geosol.

For the characterization of arsenic, cadmium, chlorine, copper, chromium, lead, nickel, vanadium, and zinc, 0.25 g samples were prepared and then digested in perchloric, nitric, and hydrofluoric acid. The obtained residue was diluted after being leached with dilute hydrochloric acid. The prepared sample was then analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) using Agilent instruments; the results were corrected for spectral interferences.

For the characterization of mercury, 0.50 g samples were prepared, which were digested in aqua regia for 45 min in a graphite heating block. After cooling, the resulting solution was diluted to 12.5 ml in demineralized water. A portion of the sample was treated with stannous chloride to reduce the mercury, which was then volatilized by purging with argon before being analyzed using atomic absorption spectrometry (AAS).

2.2. Mass balance

In the sintering pilot, a test using the mixture described in Table 2 was conducted. The sintering pilot consisted of a conical pot, with the smallest diameter being 270 mm and the largest diameter being 300 mm, a bed height ranging from 400 to 700 mm, and a volume ranging from 25.4 to 43.9 L. The sintering temperature was approximately 1250 °C with the air flow ranging between 100 and 160 Nm³/h. The same process adopted for the inputs was used to chemically characterize

Table 2 – Standard sinter mix adopted to mass balance.

Input	Mix %
Sinter feed 10	7.86
Sinter feed 11	13.1
Sinter feed 12	2.62
Sinter feed 14	7.86
Sinter feed 15	3.06
Sinter feed 16	4.81
Pellet fines 1	3.49
Pellet feed 5	0.87
Dolomitic limestone	9.03
Quicklime	0.67
Area cleaning material	1.10
Mill scale from operations	0.48
Steel sludge	1.08
Slag of KR process	0.25
Lump and sinter fines	7.80
Carbonaceous dust of coke plant	0.14
Steel slag	0.47
Thin limestone generated by calcination	0.35
Coke breeze	3.30
Returned fines	30.3

the products of this test (sinter, returned fines, and windbox powder).

Using the humidity and loss on ignition data, the actual entry mass of each input in the process was calculated. Understanding the input characterization data enabled the mass values of injection for each trace element to be determined. Thus, it was possible to identify the key inputs responsible for the injection of each of the elements in the sintering mixture.

Based on the characterization data and obtained mass of the products, the output masses and partition of each element were calculated. The mass emissions of trace elements were determined by subtracting the overall entry mass and masses present in the sinter, return fines, and windbox powder.

3. Results and discussion

3.1. Chemical characterization of inputs

3.1.1. Arsenic

The arsenic concentrations in the different categories of inputs are plotted in Fig. 1. The highest arsenic concentrations

were observed in the ferrous products, especially in the concentrate, for which a concentration of 19.88 ppm was observed.

When analyzing the individual samples in each category, high arsenic concentrations of 100.0 ppm and 37.7 ppm were observed in the Chinese concentrate samples 4 and 7, respectively, whereas the concentrations of the seven other Chinese concentrate samples ranged between 0.6 and 13.2 ppm. The Brazilian sinter feed contained a low arsenic concentration with only 1 of 17 samples having a higher concentration than the mean (19.0 ppm); two Chinese, two South African, and nine Australian samples contained higher arsenic concentrations. In the pellet feeds, the Chinese samples again contained the highest arsenic concentrations, with values of 65.1 and 50.8 ppm, whereas the higher index for non-Chinese samples contained more than 10 times less, 4.8 ppm for the Brazilian pellet feed 4.

3.1.2. Cadmium

Fig. 2 shows the cadmium concentration in the different categories of inputs. The high cadmium concentration in the steel-making residues (1.8 ppm) is evident, with a level at least 10 times greater than that of all the other categories. This value is easily explained by the concentration of cadmium in the mill scale from operations, 12.0 ppm.

3.1.3. Chlorine

In the comparison of the chlorine concentration among the different categories of raw materials, the steel-making residues contained 424.4 ppm. The fuels (6.7 ppm), pellets (20.0 ppm), and pellet fines (20.0 ppm) contained low concentrations compared with the other inputs, as observed in Fig. 3.

Among the steel-making residues, the main chlorine concentrators were the carbonaceous dust of the coke plant (2542.0 ppm), windbox powder (690.0 ppm), and blast furnace dust catcher powder (437.0 ppm). All the other steel-making residues contained concentrations of chlorine lower or equal to 50.0 ppm.

Among the Chinese concentrate samples, similar to the arsenic results, samples 4 and 7 had chlorine concentrations of 430.0 and 530.0 ppm, respectively.

In the pellet feeds, all the samples with chlorine concentrations above the mean originated from China (13 samples).

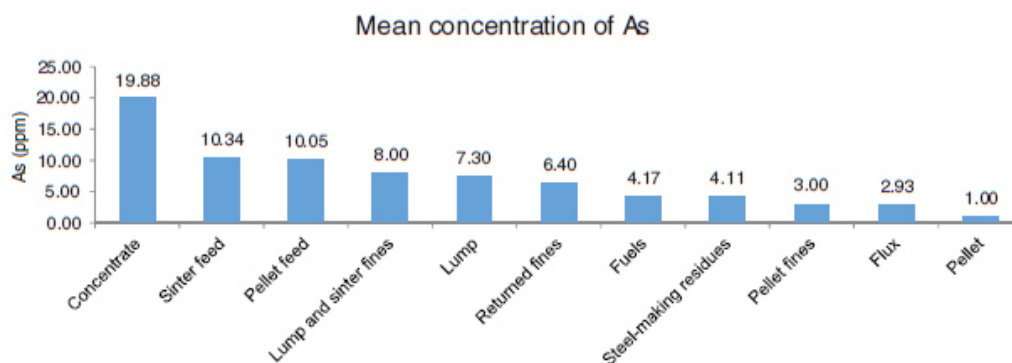


Fig. 1 – Mean concentration of arsenic in the different classes of inputs.

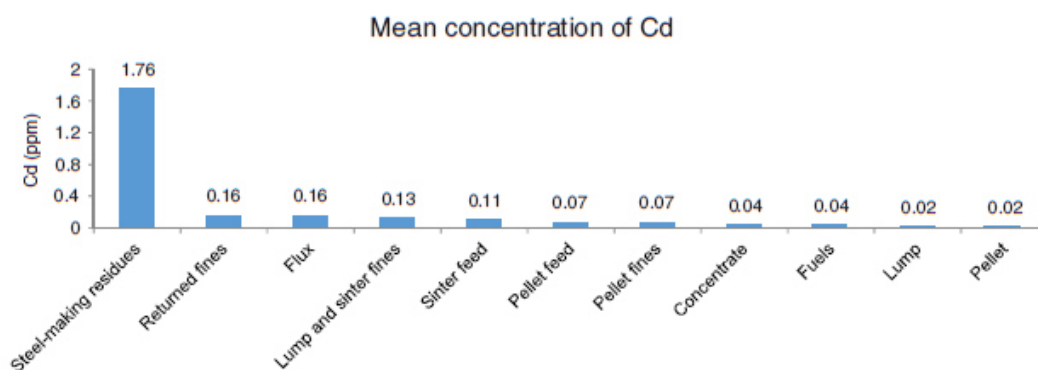


Fig. 2 – Mean concentration of cadmium in the different classes of inputs.

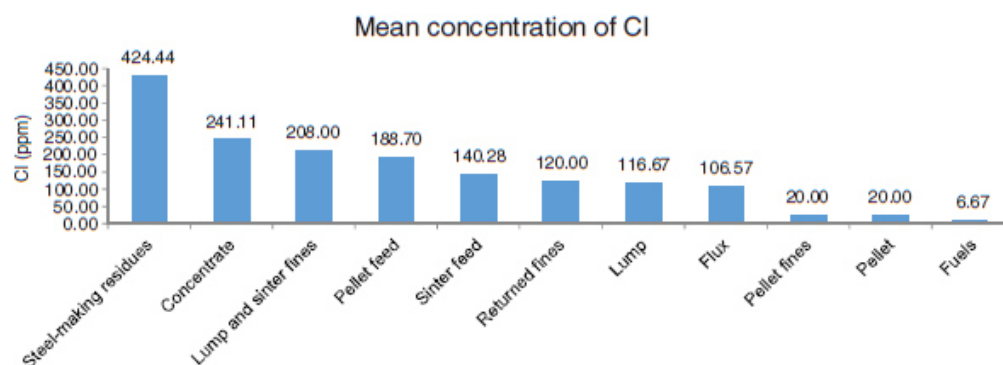


Fig. 3 – Mean concentration of chlorine in the different classes of inputs.

In the sinter feeds, the highlight was the low concentration of chlorine in the Brazilian samples, with only 1 of 17 samples having a higher value than the mean (200 ppm).

3.1.4. Chromium

Analyzing the chromium concentration in the different categories of inputs it was noted that the ores, especially the lump (40.7 ppm) and sinter feed (45.1 ppm), along with the fluxes (45.3 ppm), had a low average concentration compared with the other inputs. The highest concentration was again observed for the steel-making residues, 220.1 ppm, as observed in Fig. 4.

3.1.5. Copper

The copper concentration results for each of the categories of inputs are presented in Fig. 5. The steel-making residues had the highest copper concentration, 67.7 ppm, which was almost twice as high as the second highest copper content of 37.0 ppm.

The main component responsible for increasing the mean concentration of copper in the steel-making residues was the carbonaceous dust of the coke plant, with 360.9 ppm. All the other steel-making residues had concentrations below 50.0 ppm. In the Chinese concentrate, one sample was responsible for the high mean, concentrate 9, which

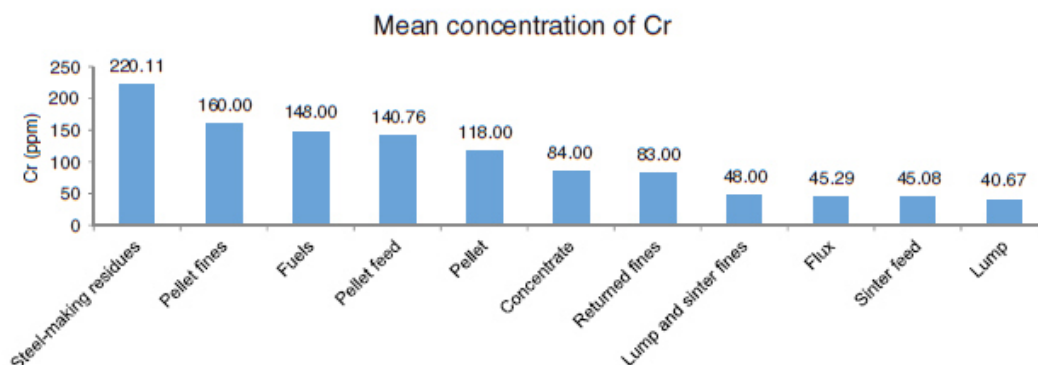


Fig. 4 – Mean concentration of chromium in the different classes of inputs.

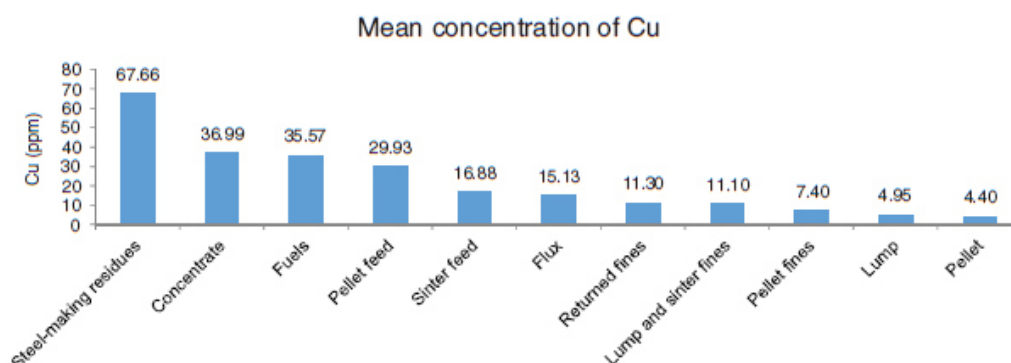


Fig. 5 – Mean concentration of copper in the different classes of inputs.

had a copper concentration of 235.0 ppm, whereas the concentrations for all the other samples only reached as high as 34.2 ppm.

Analyzing the pellet feed samples, the copper concentrations varied widely, ranging from 1.6 to 155.3 ppm. Among these samples, the Brazilian sample 1, with 103.5 ppm, and Chinese sample 9, with 155.3 ppm, had the highest concentrations.

In the sinter feed, however, two samples showed great prominence, the Brazilian sample 1, with 107.5 ppm, and the Australian sample 7, with 176.3 ppm. All the other sinter feed samples had copper concentrations below 27.3 ppm.

3.1.6. Mercury

The mercury concentration in the sintering inputs was low compared with that of the other trace elements, always below 1.0 ppm. In this context, the highest concentrators of mercury were the ferrous inputs, either as sinter feed (0.08 ppm) or pellet feed (0.07 ppm), as observed in Fig. 6.

The results of two samples stood out, the Australian sample 7, with 0.54 ppm, and the Brazilian sample 12 with 0.30 ppm. The mercury concentrations of all the other samples were below 0.15 ppm.

For the pellet feeds, all 5 Brazilian samples as well as the Canadian samples had values below the mean of 0.07 ppm, whereas the 6 Chinese samples had values between 0.10 and 0.36 ppm.

3.1.7. Nickel

Fig. 7 plots the mean nickel concentration in the different categories of sintering inputs. Among these categories, the fuel and steel-making residues stood out, with average concentrations of 135.9 and 87.3 ppm, respectively.

Analyzing the concentration of nickel in the steel-making residues, high values were observed in the carbonaceous dust of the coke plant and in the area cleaning material, with 361.1 and 200.0 ppm, respectively. The remaining residues fluctuated with nickel concentrations ranging from 10.3 to 62.0 ppm.

Among the pellet feeds, the Chinese sample 13 stood out with a nickel concentration of 349.5 ppm, a value that was approximately four times greater than that of the Chinese sample 6, which was the sample with the second highest concentration (93.3 ppm). For the sinter feeds, the highlight was the Australian sample 7, with 161.0 ppm, whereas the other samples contained concentrations at least five times smaller (less than 30.0 ppm).

3.1.8. Lead

Analyzing Fig. 8, high average lead concentrations in the fuel and steel-making residues of 273.5 ppm and 132.7 ppm, respectively, were observed compared with those in the other categories; these values are at least five times larger than those in the other categories.

In the steel-making residues, high lead concentrations of 400.0 ppm were observed in the carbonaceous dust of the

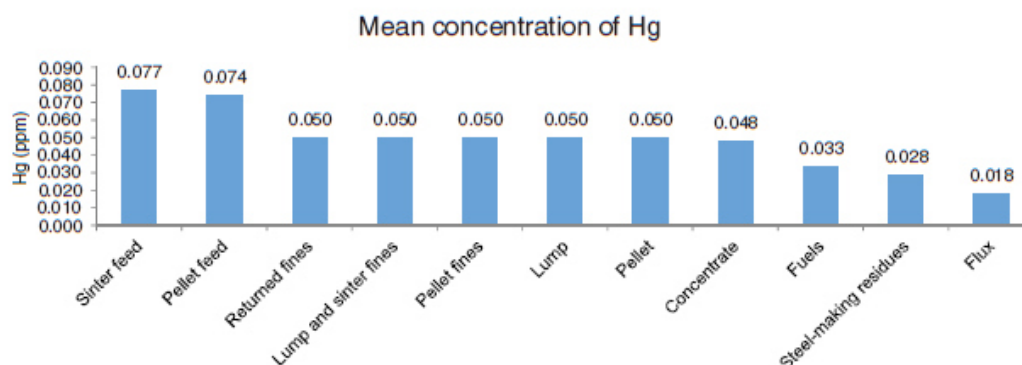


Fig. 6 – Mean concentration of mercury in the different classes of inputs.

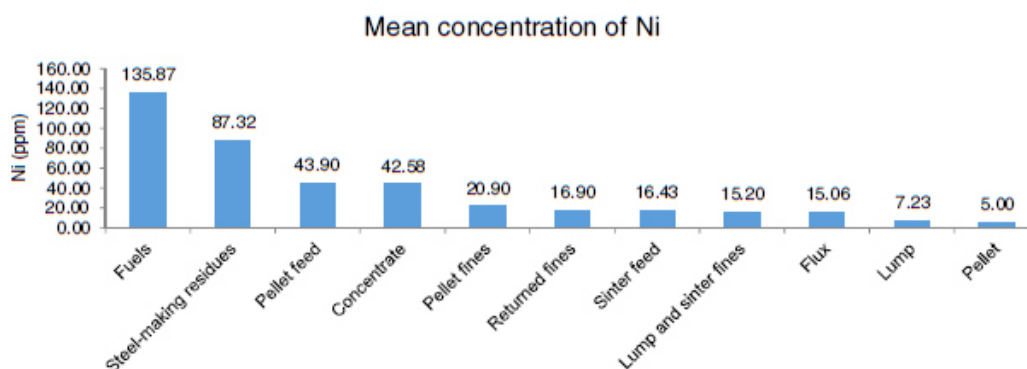


Fig. 7 – Mean concentration of nickel in the different classes of inputs.

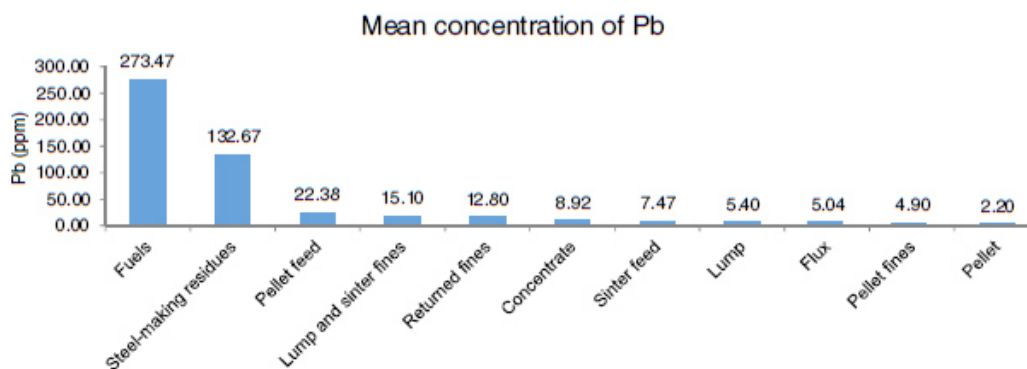


Fig. 8 – Mean concentration of lead in the different classes of inputs.

coke plant and the area cleaning material. The steel sludge and mill scale from operations also contained relatively high concentrations of 178.0 and 125.0 ppm, respectively, whereas the remaining residues had lead concentrations of less than 56.0 ppm.

3.1.9. Vanadium

Among the classes of sintering inputs, the pellet feed exhibited the highest mean concentration of vanadium (384.7 ppm), followed by concentrate (292.9 ppm) and steel-making residues (155.0 ppm). Fig. 9 shows that the fluxes and fuel contained very low levels of vanadium compared with the other inputs.

The vanadium concentrations in the pellet feeds varied widely, ranging from 0 to 2710 ppm. A large difference was also observed between the mean of the 17 Chinese samples, 500 ppm, and that of the 5 Brazilian samples, 62.6 ppm.

Among the Chinese concentrate samples, the vanadium concentration stood out in sample 1 at 1500.0 ppm. This value was almost four times higher than the second highest concentration observed for sample 7 (379.0 ppm).

Regarding the vanadium concentration in the steel-making residues, two samples exhibited significantly higher values than the others. These were the mill scale from operations (625.0 ppm) and the steel slag (470.0 ppm). All the other samples had vanadium concentrations as high as 111.0 ppm.

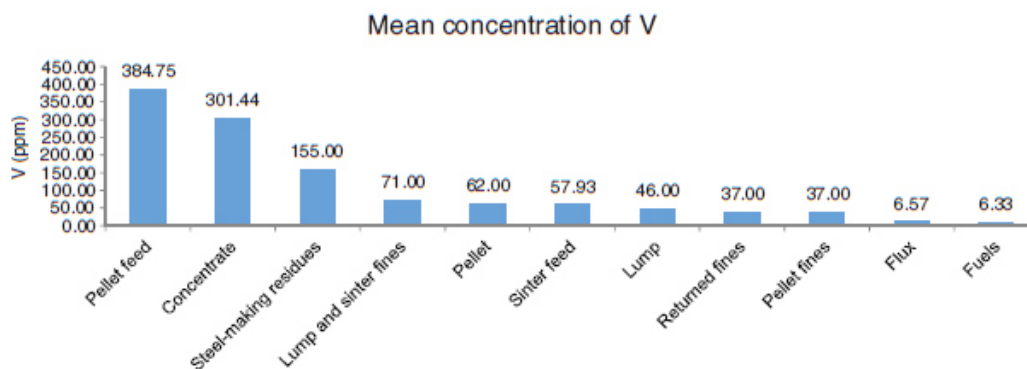


Fig. 9 – Mean concentration of vanadium in the different classes of inputs.

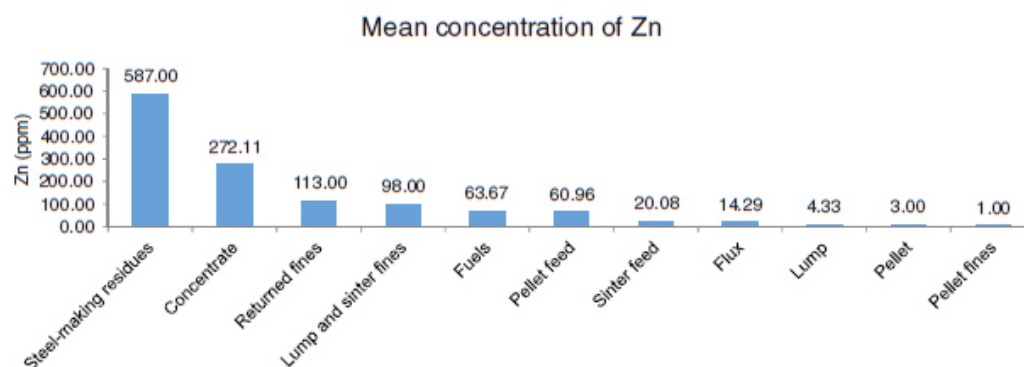


Fig. 10 – Mean concentration of zinc in the different classes of inputs.

ET	Main supplier	Partition, %			Total (g/t of sinter)
		Sinter	RFin	Emissions +	
As	Sinter feed	89%	41%	-30%	7.18
Cd	Mill scale from operations	41%	25%	35%	0.30
Cl	Fines of lump and sinter	48%	53%	0%	105.21
Cr	Sinter feed	52%	37%	11%	104.02
Cu	Sinter feed/Dolomitic limestone	51%	24%	25%	21.97
Hg	Sinter feed	50%	23%	27%	0.10
Ni	Sinter feed	42%	24%	34%	32.51
Pb	Area cleaning material/Steel sludge	48%	23%	29%	25.97
V	Fines of lump and sinter/Sinter feed	71%	30%	-1%	57.51
Zn	Steel sludge	92%	42%	-33%	125.31

Fig. 11 – Mass balance results. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

In the sinter feeds, the vanadium concentration in the Chinese 1 sample was high (823.0 ppm), a value three times higher than that of the second highest vanadium concentrator, the Australian sample 7, with 271.0 ppm. All the other samples had concentrations below 74.0 ppm.

3.1.10. Zinc

Among the sintering input categories, zinc was concentrated primarily in the steel-making residues, as observed in Fig. 10. In the steel-making residues, the mean zinc concentration was 587.0 ppm, whereas the next highest value was approximately half this value, 272.1 ppm, for the concentrate.

Among the steel-making residues, zinc appeared in higher concentrations in the steel sludge at 2568.0 ppm, blast furnace dust catcher powder at 1562.0 ppm, and area cleaning material at 624.0 ppm. All the other residues contained zinc concentrations below 210.0 ppm.

The zinc concentration in the Chinese concentrate sample 4 stood out at 1910 ppm. This value was almost seven times higher than the second highest concentration for sample 9 (282 ppm).

3.2. Mass balance

The mass balance results are presented in Fig. 11. The large intake of zinc (125.31 g/t sinter), chlorine (105.21 g/t sinter), and lead (104.02 g/t sinter) is notable.

Regarding the partitions, the elements more likely to concentrate in air emissions were cadmium (35%), nickel (34%), lead (29%), mercury (27%), and copper (25%).

Note that for arsenic, vanadium, and zinc, the mass observed in the sum of the sinter and returned fines was greater than the mass input of these elements, as indicated by the negative red bars in the table. This result can be explained by the heterogeneity of the sinter and returned fines studied.

4. Conclusions

In this study, chemical characterization of several sintering inputs in an iron ore sinter plant was performed. The steel-making residues contained the highest concentrations of trace elements (1680.1 ppm), reaching more than twice the concentration of the second highest inputs, the concentrates (772.7 ppm). Samples with high concentrations of one specific trace element showed a tendency to also contain high concentrations of other elements; for example, the carbonaceous dust from a coke plant contained high concentrations of chlorine, lead, nickel, and copper. Regarding the intake of trace elements, the elements with the highest entry masses in the sintering were zinc (125.31 g/t sinter), chlorine (105.21 g/t sinter), and lead (104.02 g/t sinter). It was not possible to achieve mass balance for some elements, indicating the presence of measurement error; the chemical characterization of each of the inputs and outputs is being performed again to mitigate such errors. Furthermore, the element partitioning suggests the manner in which their mass is distributed between the sinter, returned fines, and emissions. Because the masses of the sinter and returned fines generated in the process are much larger than the emissions mass, an element that is directed mainly for products may still be present at a higher

concentration in the emissions because of the low dilution. We also observed that the trace elements behaved in three ways during the sintering. The elements and compounds with lower vaporization temperatures volatilized and concentrated in the emissions, whereas the elements that did not volatilize during the process remained in the mixture and formed the sinter or the particles were dragged into the emissions. To understand this mechanism, future studies will be performed in a radiant furnace (with heating rates and temperature similar to the sintering process) to determine the behavior of each trace element.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors would like to thank CNPq, FAPEMIG, PROEX/CAPES, and Vale for support, and Editage (www.editage.com.br) for English language editing.

REFERENCES

- [1] União Europeia. IRIS – Industrial Reporting Information System. Bruxelas: n.d.
- [2] European Parliament and Council. 4th daughter directive relating to As, Cd, HG, Ni and PAHs in ambient air. Council of the European Union. Air Quality Framework Directive; 2004.
- [3] Milieu Ltd., Danish National Environmental Research Institute, Center for Clean Air Policy. Comparison of the EU and US air quality standards & planning requirements; 2004. p. 58.
- [4] The Economist. A small breath of fresh air. London: The Economist; 2014. Available from <http://www.economist.com/news/leaders/21595903-government-gives-its-davids-sling-use-against-polluting-goliaths-small-breath-fresh> [accessed 23.03.14].
- [5] Ministry of Environmental Protection of China. Emission standard of air pollutants for sintering and pelletizing of iron and steel industry, em GB 28662-2012; 2012.
- [6] Koniczyński J, Zajusz-Zubek E, Jabłońska M. The release of trace elements in the process of coal coking. *Sci World J* 2012;2012:294927.
- [7] Spectru Instrumental Científico Ltda. Rio de Janeiro: Spectru Instrumental Científico Ltda. Available from <http://www.spectru.com.br/Metalurgia/Nova%20pasta2/ELELIGA1.pdf> [accessed 28.04.14].
- [8] Debrincat D, Loo CE. Factors influencing particulate emissions during iron ore sintering. *ISIJ Int* 2011;47(5): 652–8.
- [9] Sammut ML, Noack Y, Rose J, Hazemann JL, Proux O, Depoux M, et al. Speciation of Cd and Pb in dust emitted from sinter plant. *Chemosphere* 2010;78(4):445–50.
- [10] Castro LFA, Figueira RM, Tavares RP. Princípios básicos e processos de fabricação do gusa ao aço líquido. Belo Horizonte: DEMET/UFMG; 2004.