

Controlling Non-Energy Emissions in a 100 Percent Wind-Water-Solar (WWS) and Storage World

In

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This document covers the following:

Carbon dioxide from chemical reaction during steel manufacturing

Carbon dioxide from chemical reaction during concrete manufacturing

All pollutants from open biomass burning and waste burning

Methane from agriculture and waste

Halogen emissions

Nitrous oxide and ammonia from fertilizers, industry, and wastewater treatment

2.4.7. Steel Manufacturing

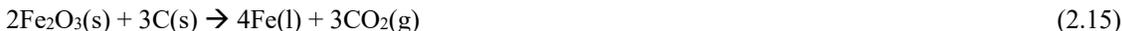
A significant use of energy as well as a source of pollution and carbon dioxide in the industrial sector is steel manufacturing. With steel manufacturing, CO₂ emissions arise not only due to the fossil fuel or biomass energy used to produce high-temperature heat but also due to chemical reaction, which releases CO₂ during the extraction of iron metal from iron ore.

Steel can be produced from raw iron ore or recycled metal. Steel produced from iron ore is produced in two stages. The first is called ironmaking; the second, steelmaking.

In the **ironmaking** step, molten iron metal [Fe(l)] is extracted from solid iron ore, also called hematite [Fe₂O₃(s)], by filling a **blast furnace (BF)** with hematite, relatively pure solid carbon [C(s)] in the form of coke (coal heated in the absence of air), and **limestone** [calcium carbonate, CaCO₃(s)]. Hot air containing molecular oxygen gas [O₂(g)] is then forced up the bottom of the blast furnace. It reacts with the coke to form carbon monoxide gas [CO(g)] and heat by



At high temperature in the furnace (up to 2,550 °C), the hematite reacts with the carbon monoxide and the coke itself to produce molten iron metal and carbon dioxide gas [CO₂(g)]:



The limestone simultaneously heats up and thermally decomposes to quicklime [calcium oxide, CaO(s)] and CO₂ by



The calcium oxide then reacts with and removes sandy (containing silicon dioxide) remnants of the iron ore to form slag [CaSiO₃(l)]



Slag is less dense than molten iron so floats on top of the iron. Slag is then cooled and removed for use in roads. Thus, traditional steelmaking releases CO₂, not only through fossil fuel and biofuel combustion to produce high temperatures, but also from chemical reaction.

Steelmaking is the second step in steel production. In this step, impurities are removed from the raw iron, and carbon and other alloying elements are added to make crude steel. Impurities removed include phosphorus, sulfur, and excess carbon. Alloying elements added include chromium, nickel, vanadium, and manganese.

Steelmaking is performed in one of two ways. **Primary steelmaking** is the use of new iron from ironmaking. **Secondary steelmaking** is the recycling of scrap steel and melting it in an electric arc furnace to produce steel.

The main method of primary steelmaking is the **basic oxygen steelmaking (BOS)** method. With this method, the molten iron and impurities from the blast furnace are mixed with scrap steel and placed in a **basic oxygen furnace (BOF)**. Oxygen is then blown through the furnace and reacts with carbon in the molten mix to form CO₂(g), which is released to the air. Calcium oxide in the molten mix also reacts with phosphorous and sulfur, the products of which rise to the top as slag and are removed. Finally, alloys are mixed in, and the molten steel is poured into pre-shaped molds, where it cools and hardens.

With secondary steelmaking, scrap metal is melted in an arc furnace. Oxygen is blown through the metal to help remove the carbon and speed the meltdown of the metal by increasing combustion. Calcium, phosphorous, and sulfur are removed and alloys are mixed in, similar to the process in the Basic Oxygen Furnace.

In sum, the sources of CO₂ during the two-step steel formation process are (a) its emissions during fossil fuel combustion to produce heat in the blast furnace and in the basic oxygen furnace, (b) its chemical release during reaction of carbon with hematite, (c) its release upon the thermal decomposition of limestone during ironmaking, and (d) its release during chemical reaction of carbon with oxygen during steelmaking. In addition, in an arc furnace, there is a small amount of CO₂ released due to the vaporization of graphite and its reaction with oxygen. The overall carbon emissions in the ironmaking plus steelmaking process using a blast furnace and basic oxygen furnace are about 1,870 kg-CO₂ per tonne-steel (Vogl et al., 2018). Of this, ironmaking produces about 70 to 80 percent of the CO₂ emissions.

2.4.7.1. Reducing Carbon Emissions with Hydrogen Direct Reduction

An alternative to extracting molten iron from iron oxide with coke during ironmaking is to extract it with hydrogen gas [H₂(g)], where the hydrogen is produced with 100 percent WWS (Vogl et al., 2018). This process is called the **hydrogen direct reduction (HDR)** process. The main extraction reaction is



This reaction occurs optimally at a temperature of around 800 °C, which is lower than the temperature needed in a blast furnace (Vogl et al., 2018). The reaction eliminates chemical CO₂ produced from the hematite reaction with carbon during ironmaking. However, an injection of carbon into the molten iron during the steelmaking process is still needed to create an iron-carbon alloy (0.002 to 2.14 percent C) to strengthen the steel. In addition, some carbon is still emitted from the thermal decomposition of limestone and subsequent emission of CO₂.

If the heat required for the HDR ironmaking process is obtained with an electric resistance furnace instead of with fossil fuels, if the hydrogen for the HDR process is produced by electrolysis (passing of electricity through water), if an electric arc furnace is used for the steelmaking process, and if all electricity is provided by 100 percent WWS, the HDR process emits only 53 kg-CO₂ per tonne of steel, or only 2.8 percent of the emissions of the blast furnace/basic oxygen furnace process (1870 kg-CO₂ per tonne of steel) (Vogl et al., 2018). The only emissions in the HDR process are some oxidation of injected carbon in the arc furnace, some CO₂ from the thermal decomposition of limestone, and some oxidation of the vaporized carbon in the arc furnace electrodes.

The system just described is a 100 percent clean, renewable energy system, but still results in a residual of 53 kg-CO₂ per tonne of steel (2.8 percent of the original emissions). The remainder will either be released to the air or captured. However, capturing CO₂ requires energy, and regardless of whether the electricity is from WWS or natural gas, it is better to use that electricity to displace a fossil fuel electricity source than to capture CO₂, since displacing a fossil fuel source eliminates not only CO₂ from the source but also air pollution and upstream mining and emissions (Section 3.6).

2.4.7.2. Reducing Carbon Emissions with Molten Oxide Electrolysis

A second alternative to extracting molten iron from iron oxide with coke during ironmaking is with **molten oxide electrolysis (MOE)** (Allanore et al., 2013, Wiencke et al., 2018). With MOE, solid iron ore, Fe₂O₃(s), is first heated in a molten electrolyte soup above 1,688 K, where it decomposes to magnetite [Fe₃O₄(s)] and oxygen by



The molten electrolyte soup contains oxides, such as silica (SiO₂), alumina (Al₂O₃), and magnesia (MgO), and has the purpose of helping electricity flow. The soup is heated further, past the melting point of pure iron, which is 1,811 K. Above this temperature, electricity is passed through the soup, producing pure molten iron by



The pure liquid iron sinks to the bottom of the cauldron, where it is drained. As such, the MOE process produces pure iron without emitting chemically produced carbon dioxide.

2.4.8. Concrete Manufacturing

Concrete is mixture of **aggregate** (sand, gravel, and crushed stone) and a paste (water and **Portland cement**). The paste binds the aggregate together, making a hard surface. Concrete is used for roads, foundations, buildings, runways, sidewalks, driveways, and a variety of other purposes.

Joseph Aspdin (1788 to 1855) of Leeds, England, invented Portland cement in the early 19th century. He formed it by burning powdered limestone and clay on his kitchen stove. Today, cement contains limestone, shells, or chalk, all of which contain CaCO₃(s), mixed with clay, shale, slate, blast furnace slag, silica sand, or iron ore. These ingredients are heated to 1,500 °C to form a hard substance that is ground into a fine, powdery cement.

The concrete industry produces about 5 percent of the world's CO₂ emissions. About half of the emissions during concrete production are from energy use and the other half are from chemical reaction during cement manufacturing. The chemical emissions rate of CO₂ from cement manufacturing is 900 kg-CO₂ per tonne-cement. These emissions arise due to the reaction,



Where the CO₂ originates from calcium carbonate. The clinker is then mixed with gypsum (CaSO₄-2H₂O) to form cement by



The cement is subsequently mixed with water to form a paste, which is combined with the aggregate to form concrete.

Three ways of reducing emissions from concrete manufacturing are to (1) use an alternative to concrete that doesn't emit CO₂ as part of the chemical process, (2) make concrete that traps CO₂, and (3) recycle concrete.

2.4.8.1. A Type of Concrete That Emits no CO₂

One commercialized alternative to concrete is **Ferrock**, or iron carbonate (FeCO₃) (Stone, 2017; Build Abroad, 2016). Ferrock is derived by first mixing waste steel dust containing iron (FeO) with crushed glass containing silicon dioxide (SiO₂), limestone (CaCO₃), kaolinite or another clay, stabilizers, promoters, and a catalyst into a mixer at room temperature. The mixture is then poured into a mold containing seawater. The filled mold is put into a curing chamber, where CO₂ from a furnace is injected. The iron, CO₂, and saltwater react together to form Ferrock and molecular hydrogen (H₂). When the final product dries, it is about five times harder than and more flexible than cement. The production of Ferrock not only avoids the chemical CO₂ emissions and most of the energy emissions of concrete production, but it also sequesters CO₂ and produces hydrogen, which can be used for other applications.

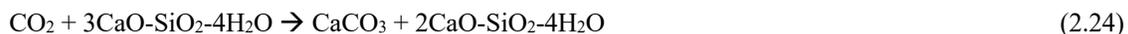
2.4.8.2. Sequestering CO₂ in Concrete

Trapping CO₂ from combustion emissions, as done in Ferrock, is a method of offsetting chemically produced CO₂ emissions from the concrete production process. Trapping CO₂ within concrete itself is another option (e.g., Carbon Cure, 2018). The clinker in cement contains CaO. When the cement is mixed with water to form a paste, the CaO reacts with water to form calcium hydroxide, Ca(OH)₂, by



If CO₂ captured from any source is mixed with the clinker, it will react to form CaCO₃ + H₂O within the cement. Upon drying, the solid CaCO₃ strengthens the cement. Even if the cement breaks, the CO₂ will not break free because it is a solid bound to the cement.

Cement also contains **calcium silicate hydrate (3CaO-SiO₂-4H₂O)**. CO₂ can react with this chemical to form calcium carbonate, which is bound in the cement, by



2.4.8.3. Concrete Recycling

A third method of reducing CO₂ emissions from concrete manufacturing is **concrete recycling**. Concrete structures or roads are often demolished. Historically, such concrete has been sent to a landfill. However, if the concrete is uncontaminated (free of trash, wood, and paper), it can be recycled. Rebar in concrete can also be recycled, as magnets can remove it. The rebar can then be melted and used for other purposes. The broken concrete is crushed. Crushed concrete is often used as gravel in new construction projects or as aggregate in new concrete.

Remaining CO₂ emitted chemically during the cement formation process could be captured chemically upon emissions. However, as stated previously, capturing CO₂ requires energy, and regardless of whether the electricity

is from WWS or natural gas, using that electricity to displace a fossil fuel electricity source is better than using it to capture CO₂, since displacing a fossil fuel source eliminates not only CO₂ from the source but also air pollution and upstream mining and emissions (Section 3.6).

2.9. Controlling Non-Energy Air Pollution and Climate-Relevant Emissions

WWS technologies address energy-related emissions. However, some emissions that affect human health and climate are not energy-related emissions but are still necessary to eliminate or reduce to decrease their impacts on human health and climate. These include open biomass burning; methane emissions from agriculture and waste; halogen emissions from leakage and draining; and nitrous oxide emissions from fertilizers, industry, and wastewater treatment. These sources of emissions and methods to control them are discussed briefly.

2.9.1. Open Biomass Burning and Waste Burning

Open biomass burning is the burning of evergreen forests, deciduous forests, woodland, grassland, and agricultural land, either to clear land for other use, to stimulate grass growth, to manage forest growth, to satisfy a ritual, by accident (campfires, debris burning, cigarettes), or by arson. About 17 percent of all global CO₂ and air pollution emissions worldwide are from open biomass burning (Jacobson, 2014). Although, such burning may be natural or anthropogenic in origin, humans cause around 93 percent of it today, and nature causes the rest (Jacobson, 2014).

Agricultural fields are often burned after harvest to remove straw leftover to clear the field for a new harvest during the next spring. Sugarcane fields are usually burned before harvest to remove the outer leaves around the sugarcane stalks to facilitate the sugarcane extraction during harvesting.

Waste burning is the burning of trash, such as in a landfill (Figure 2.34), open pit, garbage can, or backyard incinerator. Such waste burning is illegal in many countries but still occurs in many others.

Biomass burning produces not only gases that warm the climate, including CO₂, CH₄, and CO, but also climate-warming particles, including black carbon (BC) and brown carbon (BrC). BC and BrC, along with other particle components emitted during biomass burning (ash, other organic carbon, and sulfate), cause substantial health impacts to people and animals who breathe them in. In addition, the oxides of nitrogen and organic gases from biomass burning result in elevated levels of ozone, formaldehyde, and other gaseous pollutants that affect human health. Waste burning emits the same chemicals as biomass burning but also emits toxic chemicals from the burning of plastics, paints, varnishes, pesticides, medical waste, and chemical byproducts.

While some argue that biomass burning followed by regrowth of vegetation results in no net increase in CO₂ to the air, that contention is incorrect. It is incorrect because, even though CO₂ released upon burning is offset by CO₂ used to regrow the vegetation in the first place, the time lag between burning and regrowth (from 1 to 10 years for savannah and 80 years for a forest, for example, mathematically always results in elevated CO₂ in the air (Jacobson, 2004). The contention is also misleading because biomass burning emits black carbon, brown carbon, water vapor, methane, carbon monoxide, ozone precursors (organic gases and oxides of nitrogen), and heat, all of which increase global temperatures and are not recycled as CO₂ is. As such, biomass burning causes net global warming (Jacobson, 2014).

The only solution to biomass burning is to stop it. No technology exists to control its emissions. An alternative to burning agricultural waste straw is to till it into the soil. An alternative to sugarcane burning is to cut away the leafy parts of the sugarcane before harvest and mix it into the soil. Since humans cause more than 90 percent of all open biomass fires worldwide, biomass burning is largely (but not completely) preventable through government

policies restricting burning and discouraging the conversion of forest land to agricultural land or another land use type.

Similarly, the only method of reducing the impacts of landfill waste burning is to stop it because its emissions cannot be trapped. If waste is burned in an incinerator, many of its emissions can theoretically be controlled with emission control technologies; however, no technology eliminates all the emissions, including all the CO₂. Thus, even incinerators with emission controls result in significant pollution. The best control of waste burning is to eliminate it by recycling the waste or keeping it in a landfill. Waste should not be dumped into the oceans, since the plastics and many other materials do not degrade for centuries. The accumulation of plastics in the oceans has caused an environmental catastrophe, resulting in, for example, the **Great Pacific Garbage Patch**, a plastic wasteland in the middle of the Pacific Ocean between California and Hawaii that is three times the size of France.

Figure 2.34. Left: Landfill plastic waste burning in India. © cgdeaw/AdobeStock. Right: United Kingdom landfill site. Smaller pipes are carrying methane captured from under the landfill to a common larger pipe. © Angella Streluk/Wikimedia Commons.

2.9.2. Methane From Agriculture and Waste

Methane is a long-lived greenhouse gas present in the atmosphere that selectively absorbs certain thermal-infrared wavelengths of radiation, trapping some of that radiation near the surface of the Earth. It causes about 12 percent of gross global warming (Table 1.1).

Anthropogenic sources of methane include not only open biomass burning and energy-related natural gas leaks and fossil-fuel combustion, but also biological sources enabled by human activity. A 100 percent WWS energy infrastructure will eliminate methane emissions from energy production. Controls of biomass burning (Section 2.9.1) will reduce that source of methane. This section focuses on controlling methane from human-enabled biological sources.

The root biological source of most methane is **methanogenic bacteria**, which live in **anaerobic** (without oxygen) environments. Methanogenic bacteria consume organic material and excrete methane. Ripe anaerobic environments include the digestive tracts of cattle, sheep, and termites; manure from cows, sheep, pigs, and chickens; rice paddies; landfills; and wetlands. Of these, emissions from cattle, sheep, manure, rice paddies, and landfills are human-enabled emissions.

The main method of reducing methane from bacteria in digestive tracks and manure is to reducing human consumption of meat and poultry. This requires people changing their diets, which can have additional health benefits.

Methane released from **manure** can also be captured with a methane digester. A **methane digester**, or anaerobic manure digester, is an airtight tank in which manure is placed after water is separated from it. The manure is heated and stirred to simulate the inside of a cow's stomach. Methane rises from the manure to the top of the tank, where it is captured in a bag or piped out of the digester to a storage tank.

In a 100 percent WWS world, the use of captured methane should be used only for steam reforming of methane (Section 2.2.2.1) to produce hydrogen for use in a fuel cell, not for methane combustion. Whereas CO₂ emissions from steam reforming are similar to those of methane combustion, emissions of all other pollutants from steam reforming are small (Colella et al., 2005, Table 4) in comparison with those from natural gas combustion.

Methane gas from **landfills** can also be captured. **Landfill gas** is often a mixture of nearly 50 percent methane, nearly 50 percent carbon dioxide, and trace amounts of non-methane organic gases. Landfill gas is extracted by

drilling multiple half-meter-wide boreholes up to 30 m deep into a section of the landfill. Trash is then removed so that a well, which consists of a perforated or slotted siding with a cap on the bottom, can be installed. Most of the top of the well is sealed to prevent gas escape. A wellhead is installed at the top through which gas is piped to its end destination. In some cases, a network of multiple vertical and horizontal pipes can capture the landfill gas (Figure 2.34).

Once captured, the landfill gas is usually filtered to separate out the methane from the other gases. Once methane is relatively isolated, it can be used to produce hydrogen by steam reforming (Section 2.2.2.1).

Transition highlight. Rice paddies release a significant amount of methane globally, both through the leaves of rice plants and in the anaerobic environment of the flooded soil in which rice plants usually grow. On average, rice paddy soil is flooded for four months of the year. Direct seeding of rice plants, instead of transplanting them into already-flooded paddies, can reduce the time needed for flooding down to one month. This reduces methane emissions from rice paddies by 15 to 90 percent. A system of pipes can also be used to capture rice paddy methane just as it does with methane from landfill gas. The methane should be used only to produce hydrogen by steam reforming.

2.9.3. Halogen Emissions

Table 1.1 indicates that halogens are responsible for about 9 percent of gross global warming. Halogens are still used today as refrigerants, solvents, blowing agents, fire extinguishants, and fumigants. They enter the atmosphere primarily upon evaporation when they leak or when the appliances containing them are drained in a way that exposes them to the air. Their persistence in the atmosphere and impacts on warming depend on the specific global warming potential of each halogen (Table 1.2).

The main methods of reducing halogens and their impacts in the atmosphere are (a) substituting lower GWP halogens or non-halogen compounds for higher GWP halogens to perform the same function, (b) requiring more stringent standards for sealing halogens in the equipment or appliance they are used in to reduce leakage, and (c) requiring tougher standards for disposing of halogens at the end of life of the equipment or appliance they are used in. For these suggestions to be effective, they need to be implemented and enforced worldwide.

2.9.4. Nitrous Oxide and Ammonia Emissions

Nitrous oxide is a strong greenhouse gas with a high global warming potential and long lifetime (Table 1.2). N_2O is produced by bacteria and contributes to about 4.3 percent of gross anthropogenic global warming (Table 1.1). 67 to 80 percent of anthropogenic nitrous oxide originates from agriculture (Ussiri and Lal, 2012). In particular, nitrogen-containing fertilizers emit N_2O . In addition, the cultivation of legumes (plants in the pea family) results in the conversion of atmospheric **molecular nitrogen** (N_2) to N_2O , which is released to the air, but to a lesser extent than with fertilized crops. A third agricultural source of N_2O is the solid waste of domesticated animals.

Bacterial metabolism in nitrogen-containing fertilizers also results in the emission of **ammonia** (NH_3). NH_3 is a gas that dissolves in liquid aerosol particles to form the **ammonium ion** (NH_4^+), which reacts with other chemicals inside the particles. NH_4^+ inside of liquid particles also causes the particles to swell by encouraging water vapor to condense. Swollen particles reduce visibility and attract more toxic chemicals, increasing health problems for those who breathe in the aerosol particles.

Some methods of reducing nitrous oxide and ammonia emissions from fertilizers are (a) using less nitrogen-based fertilizer, (b) cultivating leguminous crops that don't require fertilizer in the crop rotation, and (c) reducing tillage to reduce the breakdown of organic fertilizer, thereby reducing reaction and release of chemicals.

The remaining anthropogenic sources of N₂O are fossil fuel combustion, open biomass burning, industrial processes, and treatment of wastewater. Transitioning fossil energy to 100 percent WWS will eliminate fossil combustion sources of N₂O. Section 2.9.1 describes how open biomass burning sources will be controlled.

The two main industrial sources of N₂O are the production of **nitric acid** for use in fertilizers and the production of **adipic acid** for use in the production of nylon fibers and plastics. To date, N₂O emissions from adipic acid production have been reduced effectively with emission control technologies in several production plants, so the expansion of such technologies to adipic acid plants worldwide will help reduce N₂O emissions. Similarly, N₂O emission control technologies for nitric acid production plants are available (NACAG, 2014) and can be implemented worldwide with stringent policies.

The source of N₂O in wastewater is organic material from human or animal waste. Modulating the dissolved oxygen content in the wastewater treatment process can control the N₂O content of wastewater (e.g., Boiocchi et al., 2016; Santin et al., 2017).

References

- Allanore, A., L. Yin, and D. Sadoway, A new anode material for oxygen evolution in molten oxide electrolysis, *Nature*, 497, 353-356, 2013.
- Boiocchi, R., K.V. Gemaey, and G. Sin, Control of wastewater N₂O emission by balancing the microbial communities using a fuzzy-logic approach, *IFAC-PapersOnLine*, 49, 1157-1162, 206.
- Build Abroad, Ferrock: A stronger, more flexible and greener alternative to concrete, 2016, <https://buildabroad.org/2016/09/27/ferrock/> (accessed November 20, 2018).
- Carbon Cure, Carbon Cure, 2018, <https://www.carboncure.com> (accessed November 20, 2018).
- Colella, W.G., M.Z. Jacobson, and D.M. Golden, Switching to a U.S. hydrogen fuel cell vehicle fleet: The resultant change in emissions, energy use, and global warming gases, *J. Power Sources*, 150, 150-181, 2005.
- Jacobson, M. Z., The short-term cooling but long-term global warming due to biomass burning, *J. Clim.*, 17 (15), 2909-2926, 2004.
- Jacobson, M.Z., C.L. Archer, and W. Kempton, Taming hurricanes with arrays of offshore wind turbines, *Nature Climate Change*, 4, 195-200, doi: 10.1038/NCLIMATE2120, 2014.
- NACAG (Nitric Acid Climate Action Group), Nitrous oxide emissions from nitric acid production, 2014, <http://www.nitricacidaction.org/about/nitrous-oxide-emissions-from-nitric-acid-production/> (accessed December 1, 2018).
- Santin, I., M. Barbu, C. Pedret, and R. Vilanova, Control strategies for nitrous oxide emissions reduction on wastewater treatment plants operation, *Water Research*, 125, 466-477, 2017.
- Stone, D., Ferrock basics, 2017, <http://ironkast.com/wp-content/uploads/2017/11/Ferrock-basics.pdf> (accessed November 20, 2018).
- Ussiri, D., and R. Lal, Global sources of nitrous oxide, In *Soil emission of nitrous oxide and its mitigation*, Springer, pp. 131-175, 2012.
- Vogl, V., M. Ahman, and L.J. Nilsson, Assessment of hydrogen direct reduction for fossil-free steelmaking, *J. Cleaner Production*, 203, 736-745, 2018.

Wiencke, J., H. Lavelaine, P.-J. Panteix, C. Petijean, and C. Rapin, Electrolysis of iron in a molten oxide electrolyte, *J. Applied Electrochemistry*, 48, 115-126, 2018.