Iron- and steelmaking processes present a largely untapped opportunity to transform some of the world’s most problematic waste streams into raw materials for production. This opportunity lies in their high-temperature environments, which offer sustainable pathways for utilizing chemical reactions to repurpose waste materials as resources, such as reducing iron oxide to iron and dissolving the carbon in waste materials into metal. High-temperature environments can be leveraged to revolutionize the role steelmakers play in globally significant, large-scale recycling, without making fundamental changes to manufacturing processes. This presentation describes the broad opportunities available to iron- and steelmakers to utilize waste streams — ranging from polymeric materials to agricultural wastes — as raw materials. The potential to implement such novel recycling solutions are not generally available to many other materials industries because they operate at relatively lower temperatures, which may not be suitable for triggering useful chemical transformations.

Recycling waste polymeric materials in steelmaking is one solution for end-of-life products, which currently impose a serious burden on overstretched landfills, as is the case with some plastics. Specifically, this lecture presents fundamental understanding of different plastic wastes — melamine, high-density polyethylene, polycarbonate and Bakelite, as well as agricultural waste and tires — and their transformations and chemical reactions at high temperatures. Plant results from EAF steelmaking in Sydney, Australia, where recycling waste is now standard practice, will also be included.

Introduction

Dr. Henry Marion Howe is most often remembered for his key role in transforming steelmaking “from an art into a science” through his exceptional powers of observation and deduction. However, another important theme also runs through accounts of his life: his boundless enthusiasm for the “possibilities” of steelmaking into the future. As C.D. King remarked in delivering the Howe Memorial Lecture in 1954, “Those who knew him well have said he derived particular pleasure from speculations on the future world of metallurgy.”¹ In this year’s lecture, I hope to honor both Prof. Howe’s dedication to “doing the science” and to thinking creatively and expansively about future opportunities for steelmakers, in light of the particular challenges steelmakers face in the 21st century.

My proposition is that today’s steelmakers have a largely untapped opportunity, not generally available to other large industries, to make a meaningful contribution to solving the world’s growing waste problem. That opportunity lies in the high temperatures we work with. We can use high temperatures to revolutionize the role steelmakers play in globally significant, large-scale recycling, without making fundamental changes to the way we manufacture steel. We can achieve this by repurposing major waste streams as raw materials for steelmaking, simultaneously reducing our own production costs and enhancing...
our sector’s environmental credentials. I am not suggesting we burn waste for energy, which is well established. What I am proposing is that we leverage high temperatures to trigger useful chemical reactions to literally reform waste materials into resources.

At University of New South Wales’ Centre for Sustainable Materials (SMaRT@UNSW), our research focuses on carbon transformation with the goal of realizing such commercially viable opportunities to transform waste. In a practical sense, that means utilizing carbon-bearing waste streams like end-of-life plastics, used tires and agricultural waste — which pose serious problems worldwide — as alternative sources of carbon. At SMaRT@UNSW, which I head, we have collaborated with OneSteel (now Arrium Ltd.) over several years in pursuit of this goal, with good results. Our commercialized polymer injection technology (PIT) allows OneSteel to substitute a meaningful proportion of coke in its electric arc furnaces with a precisely calibrated mix of granulated end-of-life polymers as a carbon injectant. The result is a novel recycling solution, which transforms problematic waste and reduces the cost of raw materials for the steelmaker. The new polymer-coke mix also improves the foaminess of the slag, and therefore, furnace efficiency. The incorporation of PIT into OneSteel’s commercial furnaces over the last five years has resulted in a 12–16% reduction in coke consumption, generated significant power savings and absorbed large amounts of waste. To date, more than 1.5 million tires have been diverted from landfills into value-added steel products.

The concept behind this proven PIT, however, has significant potential beyond this particular case study. The opportunity for steelmakers, is significantly broader. Steelmakers can transform “waste to value.” What I am suggesting is a revolution in waste recycling. High-temperature reactions offer an important addition to the environmental three “Rs” (reduce, reuse, recycle). We are now proposing a fourth “R”: reform. This is a paradigm shift in the way we think about waste materials because they can now be considered as potential raw materials that can be effectively reformed through chemical reactions into resources for industry. This is a novel, industrial-scale recycling revolution that the steel industry has the potential to lead — as long as we are willing to take on a leadership role and to recognize that waste offers a manageable, cost-effective solution to the some of the challenges we face in a carbon-constrained future. At SMaRT@UNSW, we are, in the tradition of Dr. Howe, observing various high-temperature reactions and then “doing the science” to understand how and why such potentially useful transformations occur. This paper includes fundamental understanding of different plastic wastes — melamine, high-density polyethylene (HDPE), polycarbonate and Bakelite, as well as agricultural waste and tires — and their transformations and chemical reactions at high temperatures, as well as results from EAF steelmaking process in Sydney, Australia, where recycling end of life polymers is now standard practice.

Waste to Value: Converting a Problem Into an Opportunity — The impetus for researchers and steelmakers to innovate has probably never been greater. Globally, the cost of raw materials continues to rise, while on the sales side, pressures for competitive pricing are only intensifying. Despite the world’s ever-increasing appetite for steel, producers are under pressure globally to reduce the industry’s environmental footprint. The steel industry accounts for 3–4% of greenhouse gas emissions worldwide and, on average, 1.7 tonnes of carbon dioxide are emitted for every tonne of steel produced. Meanwhile, various carbon pricing schemes are due to be implemented in 33 countries and 18 sub-national jurisdictions by the end of 2013, covering some 850 million people and around 30% of the global economy. These are clearly incompatible trends which, if we continue with business as usual, will only increase tensions for the industry. Consequently, there is an important place in steelmaking for alternative carbon-bearing materials.

Conversely, waste stockpiles — ranging from polymeric materials to agricultural wastes — are accumulating at a rapidly increasing rate, reflecting the pace of economic activity, shorter replacement cycles for goods and infrastructure, and the increasing intensity of global trade and transportation. In the U.S., the Environmental Protection Agency (EPA) reported more than 31 million tons of plastic waste generated in 2011, with a recycling rate of just 8%. In Australia, the total volume of waste generated per capita is about two-thirds that of the U.S. However, of the 1.4 million tonnes of plastic waste generated in 2010–2011, just over 20% was recycled, with the bulk going to landfill. Used tires, likewise, are not biodegradable and represent a significant and growing waste burden, with the additional complication of their potential to leach toxic chemicals into the environment. Of the approximately 20 million passenger tires requiring disposal in Australia every year, only 23% are recycled, 64% go to landfill and the remainder are dumped illegally. In some states in Australia, tires are now banned from landfill sites due to their toxicity. Worldwide, about 1.2 billion used tires are thrown away annually and 4 billion or so waste tires are currently in landfills and stockpiles, posing a risk to human health and the environment.

Yet, such waste materials consist mainly of carbon and hydrogen, elements vital in the metallurgical
industries due to their role as reductants/carburizers. These long-chain hydrocarbons consist of highly volatile matter with generally low ash content. This means steelmakers have an opportunity to use waste streams to source free or low-cost raw materials for production. The incentives for local governments and other industries to make such waste streams available for steel production are considerable, given steep landfill charges and tight anti-dumping regulations. In New South Wales, the state where UNSW is based, the gate cost for disposing of rubbish in landfill was $80.30/tonne in 2012 and is pegged to increase $10/year plus consumer price index (CPI) to drive local recycling. However, there is one common thread: the cost of disposing of many carbon-bearing wastes, which could otherwise be utilized in steelmaking, is steadily increasing.

To date, the steel industry has adopted various methods for incorporating waste materials, primarily taking into consideration the potential for energy to be released during high-temperature reactions. However, plastics have been reported as raw materials in composite ironmaking pellets. Ueki, et al. investigated reduction behavior during the heating of waste plastic materials and iron oxide composites in the temperature range of 1,000–1,300°C. Reduced iron was obtained by heating polyethylene (PE)/refuse-derived fuel and iron oxide mixtures and Ueki, et al. concluded that higher fractional reduction could be attained by increasing the temperature. Matsuda, et al. reported the reduction behavior of iron oxide by waste PE plastics and wood at temperatures of 1,200 and 1,600°C. The metal yield showed a maximum at C/O ratio ≈ 1 for a PE-hematite mixture, while the maximum C/O ratio for wood mixtures was seen to be 0.75. Polymeric materials have been considered in coke ovens as well as in blast furnaces. Shredded polymer wastes were directly mixed with the burden at NKK Japan. Stahlwerke Bremen in Germany has substituted coke, coal and heavy oils with waste plastics since 1996. Waste tires were trialed on a laboratory scale and implemented in industrial production at the Laminés Marchands Européens (LME) site in Trith-Saint-Leger, France, where they replaced part of the anthracite. Tire waste was charged from the top of the furnace into the molten bath at a rate of 1.7 kg tire per kg of carbon, while the offgases (CO and H2) levels were seen to increase by 10–20%. In developing PIT at UNSW, we focused on using the polymer material as a carbon replacement for slag foaming. In 2006, the Australian steel manufacturer, OneSteel, adopted the new technique and began replacing part of the metallurgical coke with HDPE plastic. In 2007, rubber tires were also considered for commercial reasons. A mixed blend is now injected into electric arc furnaces as standard practice in OneSteel’s Sydney and Melbourne plants and in an EAF plant in Thailand. Our current research is extending our insight into high-temperature (1,200–1,550°C) environments — with melamine, HDPE, polycarbonate and Bakelite, as well as agricultural wastes and tires. Ultimately, we aim to understand the science behind such transformations to assist industry in recognizing which waste streams have potential as raw materials and, therefore, represent new opportunities for waste-to-value processing. The research processes and some of the important results and observations discussed in this work represent the key findings in a much larger body of published work.

Experimental

Material Characteristics and Structural Transformations — To seek to understand the relative performance of waste materials at high temperatures, we used metallurgical coke and various waste streams, from polymeric materials — such as melamine, high-density polyethylene, polycarbonate and Bakelite — to agricultural wastes and end-of-life rubber tires, as carbonaceous materials. The materials vary in chemical structure and composition, ranging from thermosets to thermoplastics and woody materials, and are made up of either simple carbon, hydrogen backbones or more complex structures incorporating oxygen and/or nitrogen. Their compositions are given in Table 1.

The structural characterization of the materials was studied using x-ray diffraction (XRD) and Raman spectroscopy techniques. XRD analysis was obtained using a Philips diffractometer (MPD-Scherrer) in the UNSW laboratories. The diffraction pattern was captured at an angular range of 10–55° (2θ), a step size of 0.02 and a rate of 0.5/minute. The accelerating voltage was set to 30 kV and a current of 43 mA measured. Raman spectroscopy was used to determine the structure of melamine and PC char as a result of high-temperature treatment. Further investigation involving image analysis, using scanning electron microscopy (SEM), allowed a qualitative characterization of the samples studied.
The gas products evolved at high temperature were investigated using a wide range of instruments, from IR analyzers for CO and CO\(_2\) evolution, gas chromatography (GC) for CH\(_4\), H\(_2\) and a mass spectrometer.

**EAF Slag Reactions** — Three different types of inputs were studied: blends of coke and HDPE (with a range of input proportions), blends of coke and rubber tires (with a range of input proportions), and 100% agricultural waste. Samples were crushed in a jaw crusher and further processed in a vibrating grinder to increase uniformity in particle size, producing particles ranging from 0.45 to 0.47 mm. The blends were subjected to combustion at 1,200°C. The residual chars subsequently collected at the bottom of a drop tube furnace\(^{19}\) were then subjected to carbon/slag investigations in a horizontal furnace equipped with a high charge-coupled device (CCD) camera. The chemical composition of the industrial slag used is shown in Table 2.

Gas measurements by combined infrared gas chromatography (IR-GC) and thermogravimetric mass spectrometer (TG-MS) gas analysis allowed quantification of CH\(_4\), CO and CO\(_2\) gases.

**Formation of Ferrous Alloys**

**Solid-State Reduction:** For solid-state reduction studies, iron oxide powder with a particle size of 74 μm was blended with various wastes: Bakelite, palm shell, PU and agricultural wastes such as coconut shells. The iron oxide used was hematite, an ultrafine, chemically precipitated iron oxide produced using a synthetic rutile process, that contains primarily Fe\(_2\)O\(_3\) (85.7%), FeO (<0.1%), C (0.05%), S (0.011%). Clay was used as a binder in the pellets to improve the physical strength of the composite mix (Table 3).

The composite samples were prepared by combining powdered hematite with each palm shell, PU, Bakelite plastics, coconut shells and clay and mixing well. A small amount of water was then added to the powdered mixture to form a pliable paste suitable for formation into homogenous composite pellets. The resulting samples were left to harden and then introduced in a muffle furnace at 90°C to remove the moisture prior to the TGA-IR experiment. For this experiment, mass analysis was carried out using a TGA and the offgas analysis using an IR (for CO and CO\(_2\) analysis). A schematic diagram of the TGA can be seen in a previous study.\(^{20}\)

### Table 1

**Elemental Analysis of Metallurgical Coke, HDPE, Rubber, Bakelite and Palm Shells**

<table>
<thead>
<tr>
<th>Components</th>
<th>Metallurgical coke*</th>
<th>HDPE</th>
<th>Rubber</th>
<th>Bakelite</th>
<th>Palm shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon %</td>
<td>77.7</td>
<td>85.5</td>
<td>85.48</td>
<td>53.4</td>
<td>52.8</td>
</tr>
<tr>
<td>Hydrogen %</td>
<td>1.11</td>
<td>14.2</td>
<td>6.96</td>
<td>4.0</td>
<td>5.74</td>
</tr>
<tr>
<td>Sulfur %</td>
<td>0.28</td>
<td>0.3</td>
<td>1.68</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Nitrogen %</td>
<td>1.21</td>
<td>—</td>
<td>0.25</td>
<td>—</td>
<td>0.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>—</td>
<td>—</td>
<td>6.7</td>
<td>11.6</td>
<td>31.2</td>
</tr>
</tbody>
</table>

*Analysis performed by Amdel Laboratory and Technical Services, NSW, Australia

### Table 2

**Chemical Analysis of the EAF Slag Used in the Present Study**

<table>
<thead>
<tr>
<th>Oxide type</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>31.1</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>33.9</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>6.1</td>
</tr>
<tr>
<td>MgO</td>
<td>10.7</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>13.0</td>
</tr>
<tr>
<td>MnO</td>
<td>6.2</td>
</tr>
</tbody>
</table>

### Table 3

**Chemical Composition of Hematite and Kaolin**

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>65.4</td>
<td>SiO(_2)</td>
<td>56.2</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4</td>
<td>Al(_2)O(_3)</td>
<td>17.6</td>
</tr>
<tr>
<td>Si</td>
<td>1.4</td>
<td>LOI</td>
<td>16.7</td>
</tr>
<tr>
<td>Mn</td>
<td>0.7</td>
<td>Fe(_2)O(_3)</td>
<td>3.12</td>
</tr>
<tr>
<td>Na</td>
<td>0.3</td>
<td>CaO</td>
<td>1.04</td>
</tr>
<tr>
<td>Al</td>
<td>0.3</td>
<td>Na(_2)O</td>
<td>1.9</td>
</tr>
<tr>
<td>S</td>
<td>0.2</td>
<td>MgO</td>
<td>2.18</td>
</tr>
</tbody>
</table>
The structure of the composite pellets as a result of high-temperature reaction was investigated by the XRD analysis combined with phase identification using X’pert Highscore software.

**Formation of Ferrous Alloys:** The formation of Fe-Mn alloys using waste plastics and ferromanganese slag was studied using the sessile drop technique in a horizontal tube furnace at 1,500°C. The schematic diagram of the furnace and the composition of the manganese slag have been given in a previous publication. Rates of offgas generation as a result of ferromanganese slag and HDPE waste interaction and slag wettability on the carbonaceous substrate were investigated. Calibrated infrared cells were used to detect and measure the amount of oxides (CO and CO₂) in the gases produced. The morphological characteristics of the reacted slag were determined using FESEM coupled with energy dispersive x-ray spectrometry (EDS) analysis.

For Fe-C reactions, the waste materials were introduced into liquid metal at 1,550°C. The carbon and sulfur contents of the reacted metal were further measured using a Leco analyzer to determine the carbon pickup by the liquid metal.

### Results and Discussion

**Structural Characteristics and Transformations of the Carbonaceous Materials** — The XRD patterns showed significant differences in structure for each of the considered materials (Figure 1). Coke has an intermediate structure between graphitic and amorphous, a so-called “turbostatic” structure or random layer lattice structure. A high silica peak is seen, suggesting the presence of high ash content (Figure 1a).

HDPE is a crystalline material with sharp characteristic peaks; the linear form of PE (Figure 1b). Rubber and the Bakelite have a highly amorphous structure, showing a broad diffused spectrum with asymmetric features of (002) band (Figures 1c and 1d). Palm shell has an intermediate structure between crystalline and amorphous (Figure 1e).

![Figure 1](image)

XRD patterns of 100% coke (a), HDPE (b), rubber (c), Bakelite (d) and palm shell (e).
The structure of the melamine resin was analyzed using Raman spectroscopy. Highly graphitic features were observed due to a strong G-band (tangential) and a lower intensity D-band (disorder-induced feature). The strongest peak was attributed to the G-band, which is the characteristic peak for well-graphitized structure. The intensity of the D-band was lower, indicating a more ordered carbon structure in the graphite layer. Graphitic structures are known to have a positive effect on carbon dissolution, compared to non-graphitic structures, such as coal.

Polycarbonate (PC) polymer is a thermoplastic which has been extensively used during the last decade. PC is one of the four most problematic plastics—polyvinyl chloride (PVC), polystyrene, polyurethane and polycarbonate, which make up roughly 30% of global plastic production. In 2000, the global production of polycarbonate was 1.68 million tons, which increased to 3.41 million tons in 2010, and is expected to reach more than 6 million tons in 2020. The term polycarbonate describes a polymer, which is composed of identical units of Bisphenol A connected by carbonate linkages in its backbone chain. The molecular formula of the polycarbonate repeat unit is $\text{C}_{16}\text{H}_{14}\text{O}_{3}$ (Figure 2). Polycarbonates are strong, stiff, hard, tough, transparent engineering thermoplastics that can maintain rigidity up to 140°C and do not begin to decompose until about 380°C. Due to these properties, polycarbonates are considered engineering materials and, consequently, are extensively used in automotive, glazing, electronic, optical media, medical, lighting and appliance industries.

The initial rapid gas-phase reaction of coke-polymeric blends and polymeric materials affected the residual particles, and significant transformations were observed. The structure of the resulting carbon would be expected to play a very important role in the subsequent reactions. An ordered graphitic structure has a low degree of reactivity, while a more disordered material contains active sites represented by volatiles, which are very reactive.

Due to the increased volume of volatiles in some polymeric materials in the blend, gases would be expected to be expelled on heating via the already available pores. SEM micrographs were taken to describe the morphological transformations occurring in the palm and coconut shell structure. Ordered compact cells define the raw palm shell structure with small pores dispersed throughout (Figure 3). The cross-section of the shell shows isodiametric polygonal flattened cells with well-defined lumen arranged in a honeycomb-like pattern (Figures 3a and 3c). Coconut shells and their cross-section clearly show pore structures, which are made up of cylinder-like tubes, composed of layers of several flat sheets. Following high-temperature reactions, a progressive destruction of the cell lumen and walls rupture occurred. Removal of cell contents and, consequently, the opening of cellular structures gave rise to distinctive features with porous networks, attributed to evaporation of volatile material (Figure 4).

SEM micrographs of: raw palm shell (a); palm shell after reaction at 1,200°C (b); cross-section of the raw palm shell (c); and cross-section of the palm shell after reaction at 1,200°C (d).
metal. Faster reduction might occur due to higher amount of gases available i.e., CO and H₂ gas. A faster rate of devolatilization will release volatiles much earlier; as a result, fewer volatiles are available to sustain subsequent reactions in the slag. A slower rate allows a steady release of volatiles, promoting gasification of the carbonaceous material during subsequent reactions.

The polymeric and agricultural materials, including HDPE, rubber and palm shells, have higher concentrations of volatile matter (VM) than coke. Therefore, a further determination of the gaseous species devolatilized from polymer/coke blends during slag/carbon reactions was carried out using a GC analyzer. The chromatograms of the gases evolved were detailed in a previous publication. The HDPE and rubber polymer and its corresponding blends showed a high content of H₂. These results clearly indicate that the differences in the gases generated from plastic/coke blends arise from the differences in the chemical compositions of the polymer (Figure 5). On the other hand, the chromatograph of coke showed a significantly lower concentration of hydrogen, in accordance with the previously reported trends, which noted in-situ gas releases, for example, H₂, CH₄, from coke and/or polymers at higher temperatures.

At temperatures above 1,000°C, gas products evolving from palm shells pyrolysis were measured by TG-MS analysis. CO, CO₂ and H₂ were the main gases identified. The presence of these gases can be attributed to the lignocellulosic structure present in the palm shells, allowing for a steady gas release in subsequent carbon/slag interactions. Palm shells contain a high lignin (53.4%) and cellulose (29.7%) content, and their interactions at high temperatures are known to release large volumes of gases. Inorganic matter can also influence the formation of gas at temperature 800°C. The palm shells are expected to improve carbon/slag reactions due to the availability of gases such as CH₄+, H₂+, CO and CO₂ and other hydrocarbons. In addition, solid C and volatiles from the polymers/palm shells, i.e., CH₄ and H₂, can participate in the subsequent slag reaction, enhancing the reaction due to a faster rate of FeO reduction by H₂. As previous work has demonstrated, hydrogen increases the reduction rate by a factor of two to
three, compared to the rates of reduction by CO and CO₂.\textsuperscript{33,34}

**EAF Slag Reactions** — The experimental procedure for carbon slag reactions involved: (1) reactions in a custom-made horizontal furnace capable of reaching 1550°C, (2) visual observation using a CCD camera, and (3) off-gas analysis. Details are published elsewhere.\textsuperscript{35}

As the study introduced more complex materials, polymers and palm shells, the reactions occurring at the slag/carbon interface were expected to be affected by the presence of an increased level of hydrocarbons that could further decompose into carbon and hydrogen-bearing products. When put in contact with an iron oxide-rich EAF slag, the presence of iron oxide leads to a reduction reaction depending on the reducing agents, including C, CO and H₂ released at high temperatures. The gases produced (CO, CO₂, CH₄, H₂O, H₂) allow the slag to foam.

The rate of gas generation following the interaction of the HDPE-coke blend was reported to be the fastest, followed by the rubber-coke blends. The lowest rate of gas generation was observed when coke alone was the carbon material.\textsuperscript{35} The high volume of CO and CO₂ generated when HDPE and rubber replaced part of the coke can be attributed, to a certain extent, to the volatiles in the carbonaceous mixture. These volatiles are predominantly CH₄ gas, which, at the temperature of the tests, transforms into CO and H₂.\textsuperscript{19,29,35}

Gas entrapment in the slag phase was quantified through slag volume measurements.\textsuperscript{36} A few representative dynamic images of the slag droplet in contact with metallurgical coke (MC) and its blends with rubber, HDPE and palm char are shown in Figure 6 to qualitatively demonstrate the slag foaming behavior. The size of the slag droplet in contact with MC decreased with reaction time. HDPE blend showed significantly higher levels of gas entrapment, and rubber also showed increased volumes over time compared to coke.

To quantify the changes in slag volumes attributed to the formation, entrapment and release of gases, $V_t/V_0$ was calculated and plotted as a function of time (Figure 7). Rubber/HDPE blends and palm shell showed an increased slag volume compared to coke. The HDPE blend revealed significantly higher volume ratios as a result of increased gas generation and entrapment. The volume ratio, $V_t/V_0$, of the EAF slag reacting with metallurgical coke recorded an initial value of 1.0; with time, it decreased without any major fluctuations to 0.5. This indicates a lower extent of gas entrapment by the slag. For the rubber blend, the slag volume ratios showed significantly different trends with much higher levels of droplet volumes (Figure 7a). The palm char showed fluctuations, with the drop volume continuously growing and decreasing, however maintaining a higher volume compared to coke. The kinetics of reduction when HDPE partially replaced coke is reported elsewhere.\textsuperscript{29}

Cross-sections of the slag droplet after interaction with the waste stream containing carbonaceous blends are shown in Figures 8a and 8b. The EAF slag in contact with coke shows a limited number of gas bubbles (dark spots), whereas the slag in contact with the rubber-coke blend and palm char reveals gas bubbles dispersed in the slag matrix.\textsuperscript{32}

**Formation of Ferrous Alloys**

**Investigations on Solid-State Reduction:** Bakelite/PS/PU/coconut hematite-containing iron oxide pellets were reduced in an electrically heated, laboratory-scale horizontal tube furnace at 1,200°C in argon atmosphere. A more detailed study on Bakelite-hematite pellets will be the focus of a future paper. However, macro views of the reduced composite
Volume ratio of 100% MC–rubber blend (a); 100% MC–HDPE blend (b); and 100% MC–100% palm shell (c) interacting with EAF iron oxide slag as a function of time.\textsuperscript{38}

Cross-sections of the slag droplet after interaction with the carbonaceous substrate containing: metallurgical coke (a) and palm char at 1,550°C (b).\textsuperscript{32}
pellets can be reported here. They showed Bakelite-hematite pellets maintaining a roughly spherical shape. Small cracks were seen on the surface; however, the pellet structure remained intact. Reduced PU-hematite pellets were seen to have shrunk in mass and were relatively hard and strong. The reduced coconut-hematite pellets were also found to be hard and strong, and the surfaces of the pellets were relatively smooth. The reduced coconut-hematite and Bakelite hematite pellets had smaller cracks than the PS pellets (Figure 9).

An XRD pattern of reduced iron oxide by Bakelite, PU, PS and coconut shell is shown in Figure 10. Bakelite- and PU-containing pellets displayed a larger extent of reduction from hematite to iron compared to the other two samples, as is evident in the relatively strong iron peaks in the reduced pellets.

Bakelite-based pellets display the greatest degree of reduction with significant iron peaks, while oxide contents are quite low. Coconut and PS composites with hematite show quite similar XRD pattern, with both of them showing relatively low iron and much greater FeO content as compared to Bakelite.

**Formation of Fe-Mn Alloys:** The formation of ferroalloys was investigated through the reduction of MnO in ferromanganese slag by blends of coke and HDPE. The offgases were monitored and coke showed CO₂ as the dominant component with low amounts of CH₄. However, the gas generation behavior when the slag is reduced by the HDPE blends showed significantly reduced concentrations of CO₂ in the offgas. The decrease in CO₂ emissions coupled with the massive amounts of both CO and CH₄ proved to be an indication that the polymer undergoes thermal decomposition to liberate significant amounts of CH₄. It was further inferred that the increased levels of CO could be attributed to reduction of MnₓOᵧ by CH₄, achieved in the presence of blends containing HDPE.

**Formation of Fe-C Alloys:** Carbon dissolution into liquid iron for different waste streams has recently been determined as part of our wider research program.

We investigated the influence of the structural changes that resulted from high-temperature processing on carbon dissolution.
The melamine char was put in close contact with iron chips at different carburization times, i.e., 2, 10, 20 and 45 minutes in crucibles primarily composed of zirconia (51 wt. %), silica (39 wt. %) and alumina (3.7 wt. %). The carbon concentration in liquid iron when using melamine char attained a value of 5.65 wt. % after 45 minutes of reaction at 1,600°C. Melamine developed a high level of crystallinity according to Raman features of the carbonaceous residue.

The source of polycarbonate (PC) used in the study was CD waste. The XRD of raw CD showed a characteristic XRD pattern of polycarbonate plastic. The diffraction profiles for the char derived from waste CDs showed the presence of prominent (002) peak around ~25°, which is attributed to the presence of graphitic carbon in residue (Figure 11). The peak at 2θ angle of ~44° can be assigned to (101) diffraction of hexagonal graphene carbons. The remaining peaks at around 35°, 42° and 50° are due to the presence of residual matter in char. Aromaticity is used to describe carbon atoms in aromatic rings versus aliphatic side chains. The strong (002) and (101) peaks suggest the presence of crystalline graphitic carbon in waste CD char. The (002) and (101) peaks are due to the presence of π bonds between carbon (sp² hybridized) atoms corresponding to the presence of graphitic carbon (aromatic nature) and hence (002) peak is usually known as π band. The less-intense γ band at ~22° indicates the presence of non-graphitic carbon (aliphatic nature) corresponds to the presence of disorder in the lattice structure of graphitic carbon. But relatively lower intensity of γ band indicates the presence of reduced levels of disordered carbon.

The crystalline size in the char of the carbon structure was observed with sharp C (002) peak. The crystallite height (Lc) corresponding to C (002) peak was calculated by Scherrer formula:

\[ L_c = \frac{k\lambda}{\beta \cos \theta} \]  

where

- \( \lambda \) is the wavelength of the incident x-ray radiation (1.5409 Å) and
- \( k \) is a constant equal to 0.89.

The crystallite height (Lc) corresponding to the C (002) peak was found to be 102 Å for the PC char sample. Graphite commonly has an Lc value of around 170 Å. Coals have much lower Lc values. The higher the Lc value, the higher the ordering of carbon. The transformation during pyrolysis of waste CD to highly ordered carbon structure was clearly confirmed by (002) and (101) peaks, which were not present in XRD of raw CD.

Raman spectroscopy was used to analyze the graphitic features of waste CD char (Figure 12). The Raman spectrum consists of two peaks: C–C stretching mode (G-band) peak seen at 1,590 cm⁻¹, indicating the presence of graphite structures, and D-band seen at 1,350 cm⁻¹, indicating the existence of defects in graphite structures. The ratio \( I_D/I_G \) of intensities of the two bands is used to evaluate the degree of crystallinity.
of graphitization. The \( I_d/I_g \) ratio of waste CD char was found to be 0.8, which is less than unity, indicating good graphitization in waste CD char.

The extent of graphitization in waste CD char was comparable to graphitic char obtained from melamine in our previous work.\(^{22}\) Figure 13 shows the Raman spectrum of synthetic graphite. It can be clearly seen that G-band (around 1,565 cm\(^{-1}\)) is very prominent when compared to D-band (around 1,340 cm\(^{-1}\)), and the \( I_d/I_g \) ratio is 0.08, which indicates minimal defects in the graphite. From XRD and Raman analysis, it could be concluded that waste CD char shows some extent of ordering in its structure. In our previous studies, we have focused on the use of graphite, coal and coke as carburizing materials to understand fundamentals of the carbon dissolution process.\(^{44,45}\) The carbon dissolution into liquid iron also depends on the types and properties of carbonaceous materials, their ash and sulfur content and also the percentage of residual carbon. Synthetic graphite is a highly graphitized carburizer with very low amounts of sulfur and ash, and showed maximum carbon dissolution up to 5.3% in the first two minutes of reactions. Coal, which is less graphitized and has high ash content, showed a minimal carbon pickup of 0.48% for two minutes,\(^{45}\) whereas the polymers, such as melamine and polycarbonate, under pyrolysis, produced char with high-residual graphitic carbon, promising results for carbon dissolution. Sessile drop technique was used to investigate carbon pickup from the PC char. The carbon dissolved into liquid iron very rapidly, reaching 4.12% C in two minutes.\(^{43}\)

The carbon dissolution into liquid metal depends on the types and properties of carbonaceous materials. Graphitic structures were found to have a positive effect on carbon dissolution compared to structures showing low ordering, such as those of coals. In our studies, some of the polymeric chars developed a highly ordered graphitic structure. Another factor known to influence carburization, reducing the carbon transfer into the liquid iron at the interface between molten iron and carbon, is ash. PC char has low ash, which is also an important factor that enhances carbon dissolution relative to the conventional carbon materials containing higher levels of ash.

Industrial Implementation — Industrial trials commenced during 2006 at OneSteel Sydney Steel Mill (SSM) and in 2007 at Laverton Steel Mill, Melbourne. Rubber injection is now a standard practice at both steel plants.\(^{37,38}\) The use of rubber crumbs did not require any particular modification of the furnace infrastructure or operational procedures, other than the introduction of a dedicated storage silo and polymer injection (PIT) mixing system.\(^{18}\)

A summary of the data for the trial heats clearly shows that the HDPE/rubber blend performs better than coke (Table 5). The use of polymer/coke
blends considerably reduces the quantity of injectant required, and thus reduces the amount of raw materials needed.

Other benefits recorded at OneSteel included decreased electrode consumption, decreased lime consumption and improved yield due to a 1.4% reduction of FeO levels in the slag.３７ PIT has also reduced OneSteel’s carbon footprint, lowering CO₂ emissions as a result of decreased electricity consumption (generated by coal-fired power stations). The technology also provides the opportunity to differentiate the steel produced on its environmental benefits (“greener steel”). OneSteel has conducted specific campaigns at its SSM to check sulfur pickup in the steel when injecting a rubber/coke blend. No statistical difference in steel sulfur levels was observed when injecting rubber crumbs at OneSteel.１８

Polymer injection technology was commissioned at UMC Metals in Thailand in May 2011. The improvement in slag foaming has also resulted in a 12% reduction in the total amount of injectant used per heat, as well as a reduction in furnace power-on time and an increase in the average active power.４６ Three months after initial commissioning, OneSteel returned to UMC to conduct trials with the aim of increasing the proportion of rubber in the injection blend. These trials proved successful, and a higher rubber ratio was made standard practice, with a further reduction in total injectant per heat of an additional 8%. A comparison was done of heats made using the higher rubber/coke blend, versus heats made with coke only, under controlled conditions. Heats made using the rubber blend showed clear improvement in average active power, power-on time and productivity, as shown in Figure 14.

The operational benefits experienced by OneSteel and UMC as a result of implementing Polymer Injection Technology, combined with the environmental benefit of diverting used rubber and plastics from landfills, have shown that the process of harnessing high-temperature environments to transform waste as raw materials can be a “win-win” for both EAF steelmakers and the environment.

This results reported here have shown that blends of rubber/HDPE with metallurgical coke and palm char could be used to partially replace some of the conventional metallurgical coke used in EAF steelmaking for its inject carbon requirements. The laboratory work was reflected in the industrial implementation at OneSteel, where improvements in the slag foaming behavior and furnace efficiency were seen.

### Table 5

<table>
<thead>
<tr>
<th>Injected materials</th>
<th>Specific EE (kWh/t)</th>
<th>Carbon (kg/heat)</th>
<th>FeO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>424</td>
<td>462</td>
<td>27.6</td>
</tr>
<tr>
<td>Recycled tires</td>
<td>412.4</td>
<td>406</td>
<td>26.2</td>
</tr>
<tr>
<td>HDPE</td>
<td>406</td>
<td>379</td>
<td>26.1</td>
</tr>
</tbody>
</table>

PIT implementation in UMC Thailand: key performance indicators.１８
Conclusions

Our research to date has generated new knowledge which could prove to be extremely important in the future of steelmaking. Most notably, the waste streams studied led to better, more efficient furnace operations, when combined with metallurgical coke, than the current standard practice of using metallurgical coke alone. I have outlined only a few of the possibilities, but I believe the potential for sourcing waste as a raw material is as broad as are the range of materials containing hydrogen and carbon. That means steelmakers could envisage sourcing waste streams locally, depending on local availability; some steelmakers may have easy access to palm char, others to vast mountains of particular plastics. Industries well understand the commercial benefits and convenience of locally available raw materials, as well as the significant environmental benefits of reducing the use of coke, making good use of waste in landfill, reducing transport emissions by sourcing some production inputs locally and the subsequent improvements in furnace efficiency.

However, in the tradition of Dr. Howe, we need to “do the science.” We do, of course, understand furnaces and the reactions which occur within them using conventional processing techniques. We have now established the usefulness of various waste streams in steelmaking and have already applied some of this work in developing PIT.

In the in-depth investigation reported in this paper, for waste materials — ranging from polymeric materials to agricultural wastes — the major findings are summarized as follows.

The samples considered were seen to have different structures. The rapid gas-phase reaction of coke-polymeric blends and agricultural wastes affected the residual particles, and significant transformations were observed in the structure of the particles. The gas evolution was investigated and gases were seen to be released from the waste materials. These gases were found to be key factors affecting the subsequent slag reactions.

Slag reactions were investigated and the polymeric blends proved better than coke alone when the blends were optimized, leading to better slag foaming. Rubber blends and palm shell showed an increase in slag volume, compared to coke, allowing the formation of stable foam throughout the experiment. HDPE blends revealed significantly higher volume ratios as a result of increased gas generation, entrapment and subsequent release. The presence of hydrogen and methane release from the decomposition of polymer chains at high temperatures were seen to participate in the reaction with FeO present in the slag, as a result of carbon/slag interaction, thus increasing the rate of gas evolution and reduction. Iron oxide fine particles were also put in close contact with polymer and agricultural waste residues, and a good level of reduction was observed. Investigations into the waste materials at nanostructure levels were performed, and the influence of the carbonaceous structures on dissolution into liquid metal was established.

This innovation offers an excellent opportunity to improve efficiency while having a positive impact on the environment through energy savings and the transformation of waste streams. Such research has established fundamental pathways through which polymers can be reformed as resources for iron- and steelmaking. However, as with PIT, the benefits of waste mixes depend on carefully calibrated proportions; so we need to truly understand these useful reactions to determine how to optimize new coke-waste blends. We are continuing this work with the aim of establishing a solid knowledge base to inform the industry. Given the potential to implement such novel recycling solutions is not generally available to many other materials industries operating at relatively low temperatures, this is an opportunity which could change the way we think about raw material resources for steelmaking into the future. The building of new knowledge — in partnership with industry — reflects Dr. Henry Howe’s passion for continually deepening our understanding of the science of steelmaking.

Acknowledgments
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References
3. Climate Commission, Australia.
