UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

BEFORE THE ADMINISTRATOR

In the Matter of:	)	
	)	
Carbon Injection Systems LLC,	)	Docket No. RCRA-05-2011-0009
Scott Forster,	)	
and Eric Lofquist,	)	
	)	
Respondents.	)	

DECLARATION OF JOSEPH J. POVEROMO

I, Joseph J Poveromo, declare and state as follows:

INTRODUCTION

I have been retained on behalf of Respondents Carbon Injection Systems LLC, Eric Lofquist and Scott Forster.

QUALIFICATIONS

1. I am an internationally recognized technical expert on the blast furnace process including raw materials for this process. Among my over 150 publications in this field (see attachment) I have authored three lectures in the "McMaster University Blast Furnace Ironmaking Course" on the topics of "Blast Furnace Burden & Gas Distribution", Blast Furnace Fuel Injection" and "Future Trends in Blast Furnace Ironmaking".

2. My education includes a:
   Ph.D.(1975) and M.S.(1972), Chemical Engineering, Center For Process Metallurgy, State University of New York at Buffalo; my doctoral dissertation was focused on the blast furnace process
   B.S. Chemical Engineering, Rensselaer Polytechnic Institute, 1968;

3. From 1974 through 1993 I was a Research Consultant in the Bethlehem Steel Corporation, Research Department, where I provided technical leadership for raw materials & ironmaking research & technology including sintering, blast furnace facilities and operation and affiliated iron ore facilities.

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Attachment D

4. Since 1993 I have been a consultant specializing in ironmaking and raw materials with an international clientele including steel producers, natural resource companies, engineering firms, consultancies, government agencies, etc.

5. My professional affiliations include:

   - AIST (Association of Iron & Steel Technology) successor organization to ISS,AISE: *Iron and Steel Society of AIME*: former Director and Past Chairman of Ironmaking & Process Technology Divisions, Technical Program Chairman for ICSTI' 98, Key Reader-Transactions of ISS, <u>Distinguished Member</u>
   - *Association of Iron and Steel Engineers*: Member of Iron Producing Committee, Organizing Chairman: Injection Symposium, 1996
   - *American Institute of Chemical Engineers*
   - *Eastern States Blast Furnace & Coke Oven Assoc.*
   - *Society of Mining Engineers*
   - *Iron & Steel Institute of Japan*

6. My awards and honors include the following:

   - **Special Member** – HBIA (Hot Briquetted Iron Assoc., March 2009
   - **Honorary Chairman**, COREM Pelletizing Symposium, Quebec City, June 2008
   - **Plenary Lecturer** - Fourth International Congress on Science and Technology of Ironmaking, Osaka, Japan, Nov. 2006
   - **John Chipman Award**, 2000, Process Technology Division, Iron & Steel Society, "for best paper in ISS publications"
   - **T. L. Joseph Award**, ISS, 1998, sustained contributions to ironmaking technology
   - **Invited Lecturer** - Symposium for 250th Anniversary of
   - Jernkontoret, Stockholm, Sweden, June, 1997
   - **Distinguished Member of Iron & Steel Society**, AIME, 1994 -
   - **Keynote Lecturer** - First International Congress on Science and Technology of Ironmaking, Sendai, Japan, June 1994
   - **John Farrell Award**, 1986, for service as Chairman of Process Technology Div. and Director of Iron & Steel Society
   - **John Chipman Award**, 1984, Process Technology Division, Iron & Steel Society," for best paper in ISS publications"
   - **J.E.Johnson Award**, 1981, Ironmaking Division, Iron & Steel Society," for improved furnace charging methods"

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STATEMENT OF OPINIONS AND DISCUSSION

1.   Injectants are not Burned for Energy Recovery in a Blast Furnace.

Injected materials as a source of reductants – the role of coke in the blast furnace has been outlined as follows:

Coke plays three principal roles in the furnace:

> A **fuel** providing the energy required for endothermic chemical reactions and for melting of iron and slag,

> A **reductant** by providing reducing gases for iron oxide reduction,

> A **permeable** grid providing for passage of liquids and gases in the furnace, particularly in the lower part of the furnace.

Two other chemical roles (besides the reductant role) are:

Coke is a reductant for the reduction of elements like Si and Mn.

Coke also carburizes the iron, as hot metal produced by the blast furnace is saturated with carbon according to the following reactions:

$$3Fe + 2CO \rightarrow Fe_3C + CO_2$$
$$3Fe + C \rightarrow Fe_3C$$
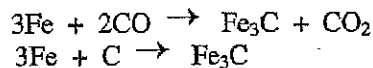
Carbon is absorbed by iron in the cohesive zone (about 1% C). As metal droplets descend through the active coke zone further carburization occurs contact with coke and carbon monoxide. The carbon level in hot metal stabilizes at about 4.5%; however, the latest research (5) suggests that this level is really dependent upon hearth conditions. This carburization role is only a minor function and accounts for only a small amount of coke consumption in the furnace, .

Additional details are available in the text from which the above is taken: J. J. Poveromo, "Coke in the Blast Furnace", lecture for the 1997 McMaster University Cokemaking Course, May, 1997, Hamilton, Ontario, also presented in May 1999, May 2003, May 2005, May 2007, May, 2011.

Role of injectants as source of reductants and not energy sources - It is worth noting that the fuel role of coke includes providing for the endothermic chemical reactions. As we will see, these endothermic reactions include the reactions whereby the injected materials are disassociated into reducing gases.

The key point of this entire case is that coke acts as an energy source in the blast furnace because it is top charged into the blast furnace. It descends in the furnace counter current to a stream of hot reducing gases. The coke is heated up during this descent to the

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raceway zone temperature of about 2800 F (1537 C); therefore when it burns in the presence of oxygen in the raceway zone, all of the exothermic heat of reaction of coke is released to the process as the primary energy source for the process. The other primary energy source for the process is the heat energy of the hot blast (blast air preheated in stoves up to 2400 F (1315 C).

The all important reason why the injectants are not an energy source is that they are injected cold into the raceway zone. The reaction of oxygen with these injected hydrocarbons ultimately produces CO and H2 gases. As noted in the attached text, it takes energy to increase the temperature of the products of these chemical reactions to the raceway zone temperature, hence the overall reaction is endothermic. Therefore the injected materials act only as a source of reductants and not as an energy source. If these materials were to be top charged to the furnace and then descend and be pre-heated by the stream of hot reducing gases, just like coke, then these materials would indeed be energy sources. However, they are not (and can never be) and so they cannot be considered energy sources.

The specific excerpts from the text "Fuel Injection in the Blast Furnace", originally from J. J. Poveromo, "Blast Furnace Fuel Injection", McMaster University Blast Furnace Ironmaking Course, Hamilton, Ontario, May 1994 follow:

"The general relationships concerning tuyere zone reactions were outlined in the previous section. The specifics of these reactions will be presented here, as follows: Injecting fuel through the tuyeres is, in effect, substituting cold fuel introduced directly into the combustion zone for some coke that is preheated during its descent through the shaft of the furnace. In addition, when a fuel is injected into the blast furnace, it can only burn to carbon monoxide and hydrogen. According to the laws of thermodynamics, it cannot burn to CO2 and H2O in the presence of carbon at the high temperatures of the tuyere zone (3200 - 4000 °F)

As shown in the table on the next page, the partial combustion of injectable hydrocarbons is exothermic at room temperature. However, it should be noted that the heat released (BTU/lb carbon) is less for any of the injectants than for the combustion of coke, and that further, the higher the hydrogen-to-carbon ratio, the less heat is released. Accordingly, methane with the highest hydrogen-to-carbon ratio of 4:1 releases the least amount of heat, as opposed to coal with the lowest hydrogen-to-carbon ratio of 0.64:1, which releases the highest amount of heat of the injected fuels. This is directly related to the heat of formation; for methane it is - 32,200 BTU/mole, as compared to - 4,800 BTU/mole for oil and only - 2,800 BTU/mole for tar and coal. It should be also noted that the total moles of combustion gases per mole of injectant combusted is greater for any of the injectants than for coke; the higher the hydrogen-to-carbon ratio, the greater the moles of combustion gases. Consequently, because the heat released by the partial combustion of injectants is less than that for coke while there are more products of combustion, there is insufficient heat to raise the temperature of the products of combustion to the temperature existing in the tuyere zone. In essence, even

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though the partial combustion of hydrocarbon tuyere injectants is exothermic at room temperature, the reactions are endothermic at the high temperature of the tuyere zone.

The above discussion relates to the hydrogen to carbon ratio on molar basis; the same relationships can also be illustrated on a weight basis: In general, the moderating effect of hydrocarbons are related to the hydrogen to carbon ratio in terms of the energy required for disassociation, as shown graphically in Figure 2 with respect to the following hydrocarbon analysis (by weight):

Hydrocarbon	H2	C	N2	H2/C
Natural Gas	22.5	69.4	8.1	0.32
Bunker "C" oil	9.3	88.6	0.3	0.10
Tar	7.1	91.4	1.1	0.08
Bit. Coal	5.0	80.1	0.0	0.06
Anthracite	2.8	80.6	0.0	0.03

Stoichiometric Combustion of Fuels Based on One Mole of Injectant

	total moles/mole C	Btu/lb C
Coke:		
$C + 1/2\,O_2 + 1.88\,N_2 \rightarrow CO + 1.88\,N_2$	2.880	3963
Natural Gas		
$CH4 + 1/2\,O_2 + 1.88\,N_2 \rightarrow CO + 2\,H_2 + 1.88\,N_2$	4.880	1279
Oil		
$CH_{1.55} + \tfrac{1}{2}O_2 + 1.88\,N_2 \rightarrow CO + 0.775\,H_2 + 1.88\,N_2$	3.655	3563
Coal Tar		
$CH_{0.65} + \tfrac{1}{2}O_2 + 1.88\,N_2 \rightarrow CO + 0.325\,H_2 + 1.88\,N_2$	3.205	3729
Coal		
$CH_{0.64} + \tfrac{1}{2}O_2 + 1.88\,N_2 \rightarrow CO + 0.320\,H_2 + 1.88\,N_2$	3.200	3729

The following table illustrates the heat effect in the tuyere zone at a hot-blast temperature of 1800 °F and a reference flame temperature of 3500 °F for coke, blast moisture, and the hydrocarbon injectants. It is assumed that coke enters at a preheated temperature of 2800 °F and air and moisture enter at the hot blast temperature of 1800
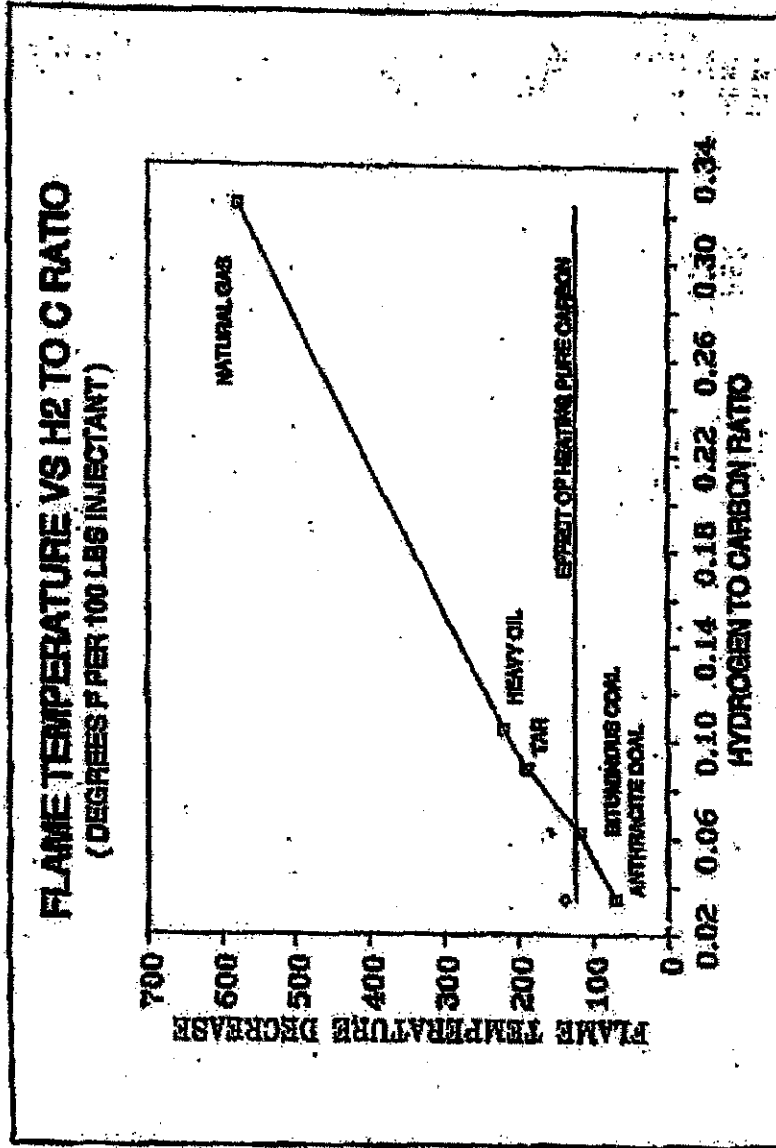

Figure 2

°F.

HEAT EFFECTS AT RAFT OF 3500 °F AND BLAST TEMPERATURE OF 1800 °F

Reactions	Heat Effect
	BTU/mole of carbon
Coke with Air	- 12,640
Coke with Moisture	+ 81,090
Natural Gas with Air	+ 83,625
Oil with Air	+ 29,530
Coal Tar with Air	+ 14,055
Coal with Air	+ 14,050

Because at the reference temperature of 3500 °F, the heat producing reaction of burning coke is exothermic by 12,640 BTU/mole of carbon, the flame temperature would rise above 3500 °F except for the balancing effect of moisture reacting with hot coke to consume the excess heat, as evidenced by the fact that at the reference flame temperature of 3500°F, the coke moisture reaction is endothermic by 81,090 BTU/mole. Alternatively, the hot blast temperature could be decreased below 1800°F to control the flame temperature at 3500 °F, but it is desirable to use the maximum hot blast temperature to displace coke and to increase production rate.

As further shown in the last table, the partial combustion of all the various hydrocarbon injectants is endothermic at the 3500 °F reference flame temperature. The degree of endothermicity is in the opposite direction as the heat released when the same hydrocarbons are combusted at room temperature. For example, natural gas, which was the least exothermic at room temperature and produced the largest amount of combustion products, is the most endothermic or has the greatest chilling effect at the reference flame temperature of 3500 °F.

Because of the endothermic effect of the injectants, one of two procedures must be followed to maintain a thermal balance; i.e., constant flame temperature in the furnace. Either the hot blast temperature must be increased or the moisture removed from the blast. Since, as stated above, it is desirable to maximize hot blast temperature, it is best to remove moisture from the blast air. As a result, the heat is no longer consumed because of the removal of the blast moisture can now be consumed by the endothermic reactions caused by the injection of the fuels. In this manner the heat balance around the tuyere zone is essentially unchanged and the furnace can continue to operate as efficiently as when coke alone was charged. In essence, when a fuel is injected, in order to maintain maximum efficiency of blast furnace operation during fuel injection, the moisture content of the blast air must be decreased to compensate for the chilling effect of fuel injection at the tuyeres and to keep the flame temperature constant.

Amount of Fuels That Can be Injected at 3500 °F Flame Temperature

Hot Blast Moisture	Fuel Injection	Total Energy at Tuyere	Tuyere Gas moles/1000 scf

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Fuel	gr/ft^3	Lb/1000 scf	BTU/1000 scf	CO	H2	Total
none	21	-	93,684	1.267	0.167	1.434
Natural Gas	8	1.425	93.920	1.163	0.241	1.404
Oil	8	3.044	92.929	1.163	0.230	1.393
Coal Tar	8	4.225	92.054	1.163	0.170	1.333
Coal	8	5.333	92,761	1.163	0.184	1.347

The above table illustrates the amounts of the various fuels that can be injected at a hot blast temperature of 1800 °F while maintaining a constant flame temperature of 3500 °F. As shown, with no injectant, flame temperature is controlled at 3500 °F with 21 grains of blast moisture. It has been assumed that the blast moisture can be decreased to an ambient level of 8 grains/scf and the amount of each of the respective fuels that can be injected at that moisture level while maintaining the constant flame temperature of 3500 °F is presented in terms of pounds of fuel injected per 1000 SCF of dry blast air. Several points are worth noting. First, because natural gas has the most chilling effect on the furnace, it can be injected in the least amount of all injectants. Conversely coal, with the least chilling effect, can be injected in the greatest amount. Further, the total energy per 1000 SCF of blast and the total moles of combustion products are approximately equal for all injectants, demonstrating further that the amount of each fuel that can be injected is based primarily on maintaining constant furnace conditions.

We can now combine the combustion and disassociation aspects to demonstrate the benefits of hydrocarbon fuel injection relative to just steam addition. When steam is injected to moderate the flame temperature it cannot avoid reacting with coke to absorb much energy at the tuyere, as well as causing a coke penalty by involving the carbon in coke in the reaction discussed above. With hydrocarbon fuel injection, less energy is consumed when compared with steam and, most importantly, the reaction does not involve the carbon in coke, but oxygen instead.

Thus, using hydrocarbons to control flame temperature has a twofold effect
1. *The hydrocarbon replaces water in the tuyere zone and eliminates the coke penalty associated with blast moisture, and*
2. *the hydrocarbon acts as a replacement for coke because it provides additional reducing gas to the process.*

As noted in the above text **"the hydrocarbon injectants acts as a replacement for coke because it provides additional reducing gas to the process"**. It does not act as an energy source

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2.   The Use of the Terms "Fuel" and Fuel Injection" Are Misleading.

Misnomers in the world of ironmaking and the ironmaking literature - the jargon of ironmaking includes many expressions that are not technically correct but are embedded in the vocabulary of blast furnace ironmaking. One such term is "slag volume". This really refers to the rate of slag generation in the blast furnace in units of kg/metric ton of hot metal or lbs/net ton of hot metal. However, the liquid slag is much less dense then the liquid hot metal being cast from the furnace and gives the impression of a large volume of material; hence the expression "volume" was developed and is still used.

Misnomer – fuel injection - Of more relevance to the current case is the term "fuel injection". The blast furnace was originally only fed with initially anthracite and then later metallurgical coke, as the source of reductants and as the prime energy source. Both of these were (and still are) top charged into the top of the blast furnace; an important distinction, as we explained above. Later, technology was developed to introduce solids (pulverized coal), liquids (oil, coal tar) and gases (natural gas, coke oven gas) through the blast furnace tuyeres (where the hot blast enters). Much of the early application of this technique involved the injection of Number 6 fuel oil, hence the term "fuel injection" became a convenient label for all injected materials. Indeed, all of these materials are considered fuels when burned in a combustion boiler setting where these materials are reacted with air (or oxygen) at room temperature. Accordingly, until the recent past, all materials being injected have been placed in the category of "fuel injection". Indeed, the lecture I will be referring up (of which I am the primary author) is entitled "Fuel Injection in the Blast Furnace" from the McMaster University Blast Furnace Ironmaking Course. The excerpts from the version cited were written for the 1994 course; the same lecture notes will be used in the 2012 edition, to be presented in May 2012. Only in the past two decades has the role of injected materials been more properly scientifically defined as a source of reductants. This has been well explained by Rorick in his declaration where he cites the published work of Jeschar and Dombrowski from the 1998 ICSTI proceedings.

3.   Injectants are a Source of Carbon in Hot Metal Produced in a Blast Furnace.

Source of carbon for carbon in the hot metal – In the testimony of expert witness Fruehan, it was stated that the carbon in the hot metal comes entirely from the coke and therefore the injected materials do not contribute to the ingredients of the final hot metal product. This statement is not correct, as in the past two decades it has become clear that indeed the injected materials are not completely reacted in the raceway zone and that unreacted (carbon) particles are consumed elsewhere in the furnace either as reductants or by being dissolved into the hot metal. This could include the carbon from the injected materials. There are ample references we could cite that show how not all injectants are reacted in the raceway region. These include, among others, papers that analyze the blast

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furnace top dust in an effort to distinguish carbon forms from coke vs. carbon forms from the injected materials.

4. Unitene LE and Unitene AGR are Suitable for Use As Injectants in a Blast Furnace.

The Unitene products contain over 97 % hydrocarbons so they are eminently suitable as reductant replacements for coke in the blast furnace. The available MSDS information suggest minimal amounts of other elements that can be readily accommodated in the blast furnace process.

5. The JLM Column Bottoms Are Suitable For Use As Injectants in a Blast Furnace.

The JLM carbon bottoms are rich (over 95 %) in carbon and hydrogen so they will supply the reductants needed to replace a portion of the coke used as reductant. Another major component is oxygen that will help to form the reducing gas CO. Other elements present at less than 1.0 % include Na, K, S and ash components (SiO_2, Al_2O_3, Cao, MgO, TiO_2, S, Fe, etc) are all in small enough proportions to be readily accommodated in the blast furnace process. Metals and trace elements are all below 1 ppm and so pose no issues. The moisture content of < 2 % is also quite acceptable

Pursuant to 28 U.S.C. Section 1746, I declare under penalty of perjury that the foregoing is a true and accurate statement of my opinions in this matter.

Dated: March 29, 2012   *Joseph J. Poveromo*

                                Joseph J. Poveromo, PhD
                                1992 Easthill Drive
                                Bethlehem, PA 18017