

Reduction of FeO in EAF Steelmaking Slag by End-Of-Life Polystyrene and It's Blend with Metallurgical Coke

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ABSTRACT

The reduction of FeO-containing slag by end-of-life polystyrene (PS) and its blend with metallurgical coke has been investigated through experiments conducted in a laboratory scale horizontal tube furnace. Composite pellets of EAF slag (47.1% FeO) with PS, coke and a blend of PS/coke (in the ratio PS:Coke =3:2) were heated rapidly at 1550 °C under high purity argon gas and the off gas was continuously analysed for CO and CO₂ using an online infrared gas analyser (IR). The extent of reduction after fifteen minutes, level of carburisation, extent of desulphurization and the ease of metal/slag separation were determined for each carbonaceous reductant. The results show that FeO can be effectively reduced from EAF slag to produce metallic iron using end-of-life PS and its blends with coke as reductants; improvements in the extent of reduction, ease of metal/slag separation, level of carburisation and extent of desulphurisation of the reduced metal were observed when coke was blended with PS.

Keywords – FeO reduction, metallurgical coke, polystyrene, carburisation, desulphurisation

I. INTRODUCTION

Only 27.1% of 27,738 tonnes of postconsumer PS was recycled in Australia in 2010-2011 [1]. The rest was either landfilled or dumped illegally. Although this recycling rate is still higher than the corresponding rates for plastics like polyurethane (7.2 % of 51,934 tonnes) [1] and nylon (5.3% of 18,884 tonnes) [1], the impact of waste PS on landfill sites is still high and there is a limit to which it can be recycled mechanically. PS is a synthetic aromatic polymer made from the monomer styrene (C₈H₈), a liquid petrochemical. It is one of the most widely used plastics, the scale of its production being several billion kilograms per year[2]. It is very slow to biodegrade and therefore a focus of controversy, since it is often abundant as a form of litter in the outdoor environment, particularly along shores and waterways. PS contains carbon (~92 wt %) and hydrogen (~8 wt %) and its thermal decomposition at high temperatures could generate large amounts of the gaseous reducing species H₂ and CH₄ (which are known reductants of metal oxides) similar to what has been reported for other postconsumer plastics [3-6].

The use of waste polymeric materials as chemical feedstock in iron and steelmaking is a relatively new concept that has not been widely investigated. Moreover, most of the research on the reduction of iron oxides has focused on the use of carbon (in the form of graphite or metallurgical coke) as a reducing agent. Apart from acting as a chemical energy source, PS can also be used in blends with coke to induce slag foaming in the EAF, owing to its

high volatile matter content. Rahman *et al.*[7] investigated the use of coke/waste plastics blends in EAF steelmaking and concluded that the addition of plastics improved slag foaming behaviour. Sahajwalla *et al.*[8] investigated the combustion of organic wastes for use in EAF steelmaking and showed that blends of coke with end-of-life rubber tyre (RT) and PP had higher combustion efficiencies than coke alone. Dankwah *et al.*[3-6] investigated the reduction of FeO in EAF steelmaking slags using blends of coke with high density polyethylene (HDPE), RT, polyethylene terephthalate (PET) and PP respectively, as reductants and proposed that the hydrogen and fixed carbon contents of a carbonaceous material are important for improved rates in reduction and carburisation.

Not much is known about the use of PS as a reductant or carburiser in iron and steelmaking technologies. Accordingly, in this work, the potential feasibility of PS and its blend with coke to function as reductant and carburiser is investigated through the composite pellet approach. The effect of PS addition on the following is also investigated:

- extent of reduction of FeO in EAF slag by coke
- degree of carburisation and content of sulphur in the reduced metal

II. EXPERIMENTAL PROCEDURE

2.1 SAMPLE SELECTION

Metallurgical coke, PS and a blend of PS with coke (in the ratio PS:Coke =3:2) were employed

in this study as reductants. Two types of PS were used in this investigation; Styron 685 (PS 685) and Styron 470 (PS 470). The chemical composition of the samples and the ash analysis are given in Tables 1 and 2 respectively. Unlike metallurgical coke, PS produced negligible amount of ash, so ash analysis was performed only for coke. An EAF slag obtained from OneSteel Sydney Mill, NSW, Australia and having basicity (B3) of 1.66 was utilised as the source of iron oxide; its XRF composition after removal of residual iron with a magnet is given in Table 3.

Table 1: Chemical composition of coke and PS

Component	Coke (wt %)	PS (wt %)
Moisture	4.60	Nd
Volatile Matter	3.0	Nd
Ash	18.3	Nd
Total Carbon	78.7	92.26
Fixed Carbon	71.7	Nd
Hydrogen	1.11	7.74
Sulphur	0.32	Nd

Nd: Not determined

Table 2: Ash analysis of coke

Component	Coke (wt %)
SiO ₂	50.7
Fe ₂ O ₃	4.8
Al ₂ O ₃	36.0
TiO ₂	1.4
P ₂ O ₅	1.6
CaO	3.3
MgO	0.94
K ₂ O+Na ₂ O	0.92
SO ₃	0.39

Table 3: Composition of EAF slag used

Component	Composition (wt %)
CaO	24.1
FeO	47.1
Al ₂ O ₃	4.9
SiO ₂	9.6
MgO	10.2
MnO	4.8
Basicity B3 = % CaO/(% SiO ₂ /% Al ₂ O ₃)	1.66

2.2 SAMPLE PREPARATION

2.2.1 THERMAL DECOMPOSITION STUDIES

Samples of metallurgical coke were ground and sieved to particle size in the range of -470 +450 μm while samples of granulated PS were crushed to smaller sizes by using a cutting mill “Pulverisette 15” (Fritsch GmbH, Idar-Oberstein, Germany). By means of a sieve insert with 0.5 mm trapezoidal perforations in the cutting mill a particle size -470 +450μm,

similar to that of metallurgical coke was obtained. The hydrocarbonaceous materials (PS and coke-PS) were mixed thoroughly with alumina powder (-150 μm) and cylindrical pellets were formed from the resulting mixture by applying a load of 7.5 tonnes for 1 minute in a hydraulic press. The use of alumina powder was to slow down the decomposition process (to enable gas measurements by the IR analyser) as well as mimic the reduction environment through the cylindrical pellets. The alumina powder acted as a blank medium, since its reduction will be difficult at the selected temperature.



Fig. 1: Composite pellet (of Al₂O₃ + PS) utilized for thermal decomposition of PS at 1550 °C

2.2.2 REDUCTION STUDIES

The slag-carbonaceous blends were compacted in a die to produce cylindrical pellets (11.0-11.2 mm thick and 14 mm diameter), (Fig. 2), by applying a load of 7.5 tonnes for 1 minute in a hydraulic press. Coke-PS possessed self-binding properties and, accordingly, did not require the addition of any binder.

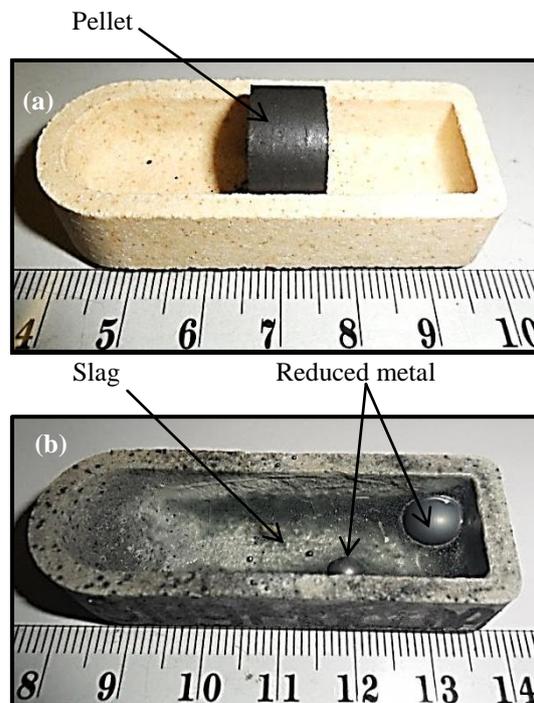


Fig. 2: Composite pellet (slag + PS): a) before reduction and b) after reduction at 1550 °C

The mass of the composite pellet was fixed (~4.77 g) and it was comprised of ~ 3.83 g slag and ~ 0.94 g carbonaceous blend so as to have a C/O molar ratio ranging from 2.44 to 2.87. This ensures that excess carbon is available in the system to allow for the reactions to reach completion as well as restrict the content of H₂O in the off-gas to negligible levels. In this ratio 'O' refers to the oxygen content of the FeO in the slag while 'C' refers to the total carbon from coke and PS in the blend.

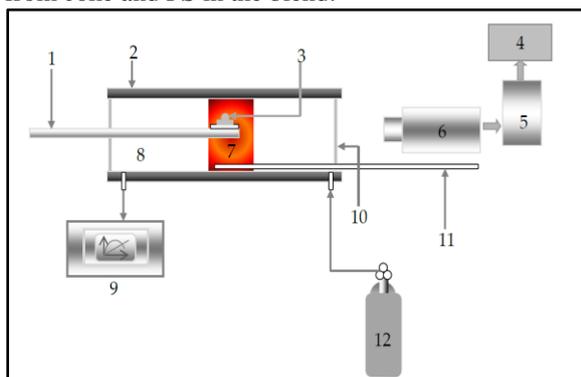


Fig. 3: Schematic of the horizontal tube furnace and IR gas analyser system.(1 Sample Rod; 2 Alumina tube; 3 Reaction mixture; 4 PC; 5 DVD; 6 CCD Camera; 7 Hot Zone; 8 Cold Zone; 9 Gas analyser; 10 Quartz window; 11 Thermocouple; 12 Argon gas)

2.3 EXPERIMENTAL PROCEDURE

2.3.1 THERMAL DECOMPOSITION EXPERIMENTS

The experimental apparatus consisted of two gas analysers connected to an electrically heated horizontal tube furnace and a data logging computer (Fig. 3). CO, CO₂ and CH₄ were monitored continuously by an IR gas analyser (Advance Optima model ABB® AO2020) while a GC analyser (SRI 8610C Multiple Gas Chromatograph #3 configuration, equipped with a thermal conductivity detector, TCD) monitored H₂, H₂O and C_nH_m. The furnace was purged continuously with argon gas (99.995% purity) to ensure an inert atmosphere. The furnace was preheated to the desired temperature and the sample was inserted; gas measurement commenced immediately after insertion and continued for 30 minutes. No appreciable change in gas composition was observed beyond 30 minutes

2.3.2 REDUCTION EXPERIMENTS

The reduction experiments were conducted in a similar way as the thermal decomposition process, except that composite pellets in this case contained slag instead of alumina. After the furnace had attained the desired hot zone temperature, the sample was pushed into the reaction hot zone and gases were monitored for 20 minutes.

III. Results and discussions

3.1 Thermal decomposition behaviour of PS at 1550 °C

The thermal decomposition behaviour of PS at 1550 °C is illustrated in Figs 4 and 5. Two distinct features are noticeable from the thermal decomposition of PS:

- The generation of large amounts of CH₄, relative to CO and CO₂
- The generation of hydrogen, indicated by the sharp peak in Fig. 5

Thus thermal decomposition of PS generates the gaseous reducing species CH₄ and H₂ into the reaction environment; this may enhance the overall reduction process.

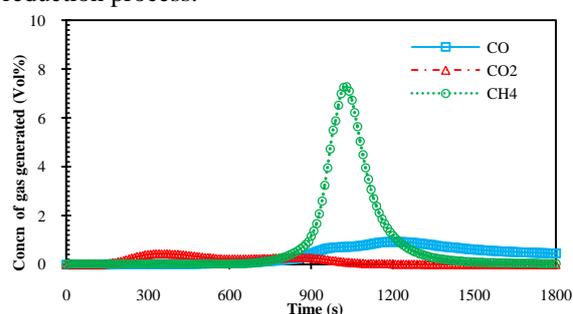


Fig. 4: Gas generation behaviour during the thermal decomposition of PS from a PS-alumina compact at 1550 °C

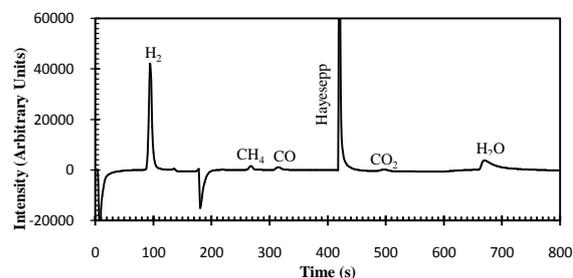
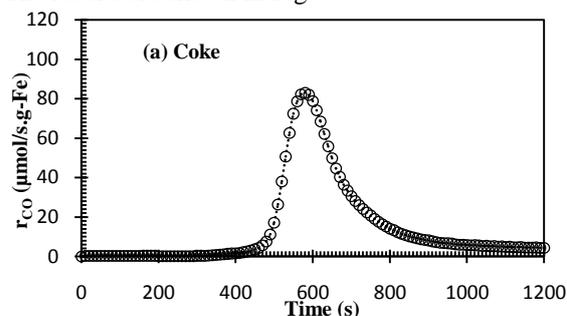


Fig. 5: Gas chromatogram obtained after 60 s of heating PS-alumina compact at 1550 °C

3.2 GAS GENERATION RATES (IR ANALYSER)

The amount of CO removed from the slag was calculated using the off-gas data for each blend. The results are shown in Fig. 6.



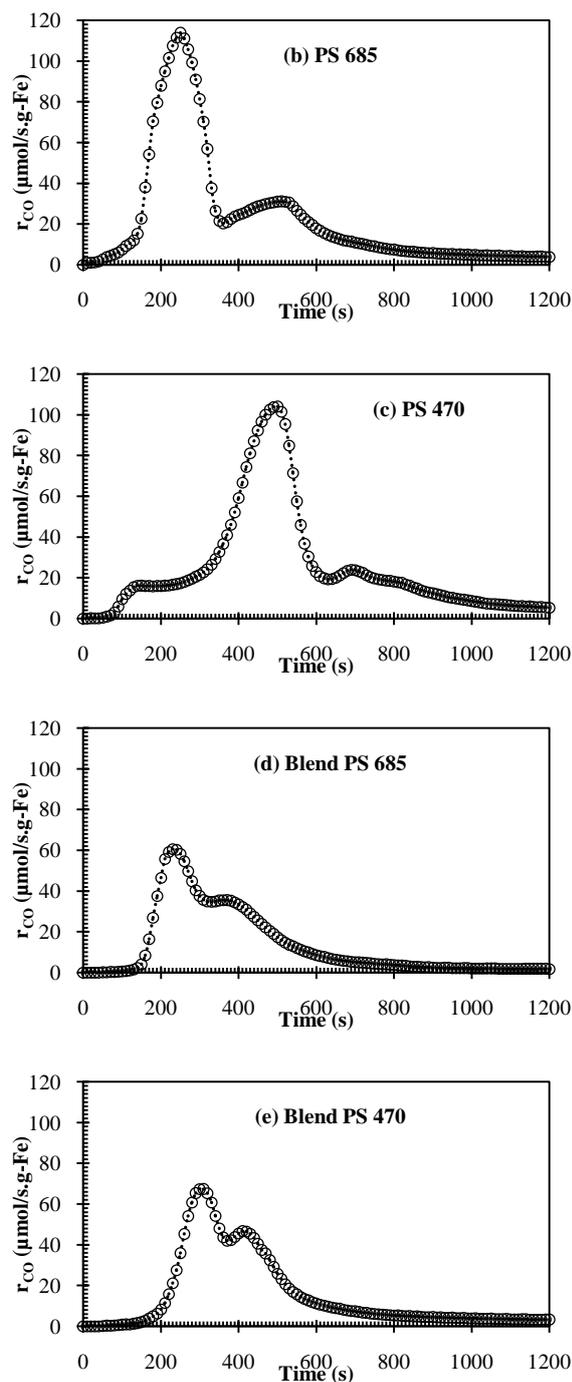


Fig. 6: Rate of CO generation as a function of time during the reduction of FeO in slag by each reductant at 1550 °C

The rate of CO generation for PS 685 and PS 470 became significant almost immediately and after 60 seconds, attaining their maximum values after 410 seconds. A minor peak occurs at 510 and 690 seconds for PS685 and PS 470, respectively, an indication that both carbon and hydrogen from PS partake in the reduction process. CO generation by PS and the blends occurs much faster than by coke alone

in the first 400 s, with the highest peak (maximum rate of CO generation $\sim 113.88 \mu\text{mol/s.g-Fe}$) being achieved for PS 685. On comparing the amount of gas generated by coke with the blends (Fig. 6) it can be observed that, although the amount of fixed carbon decreased, the total amount (mol) of CO generated by each of the blends after 900s was higher than that by coke. Although the rates of CO generation differ, we notice the striking similarities in the shapes of the graphs for the raw polymers PS 685 and PS 470 and also for the blends, Blend PS 685 and Blend PS 470. This should not come as a surprise since the two carbonaceous reductants were synthesized from the same parent monomer C_8H_8 . At this stage it is difficult to explain the observed differences in CO generation rates between PS 685 and PS 470 and also between Blend PS 685 and Blend PS 470. The CO generation observed in this investigation was for a single pellet; in industrial RHF processes with multiple layers of pellets this CO could act along with H_2 and CH_4 from pellets at lower layers as reductants for pellets in upper layers which are at higher temperatures as was observed by Hasegawa *et al.*, [9].

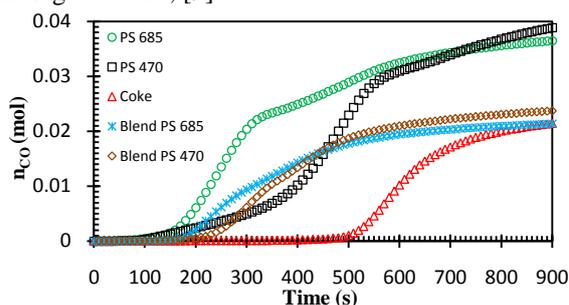


Fig. 7: Comparison of accumulated amounts of CO generated by coke, PS and coke-PS blends at 1550 °C

3.3 EXTENT OF REDUCTION

The reduced metal was weighed and the content of oxygen was determined using a LECO Nitrogen/Oxygen analyser (model TC-436 DR 602-500-600, LECO Corporation, Michigan, USA). The extent of reduction was determined from the calculated oxygen values along with the CO and CO_2 from the off-gas, with the knowledge that the initial concentration of removable oxygen from the reducible component of the slag (FeO) is about 22.27%. The extent of reduction, f , was plotted as a function of time for coke, PS, and the blends. The result is illustrated in Fig. 8. From Fig. 8, reduction by coke progresses rather poorly in the first ten minutes, probably due to its high ash content which could affect reduction; blending with the polymer appears to improve reduction significantly with extent of reduction increasing from 51.9 % for coke to 92.6% and 93.9% for Blend PS 685 and Blend PS 470, respectively. Within this period, reduction

activity is complete for the polymer (both PS 685 and PS 470). This improvement in reduction is attributed to the extra reducing gases H₂ and CH₄ made available in the system through the thermal decomposition of PS. In particular, H₂ apart from being a faster reducing agent than both CO and solid carbon enhances the rate of reduction of iron oxides by CO [10,11] when it is added to a reduction system containing the latter. The CO₂ and H₂O produced from the reduction of iron oxide gasify any available carbon at high temperatures to generate more reducing species (CO and H₂). Accordingly, a series of cyclic reactions [12,13] is set up, as the CO and H₂ (products of carbon gasification) in turn partially react with the FeO and further reactions continue. These cyclic reactions persist until all the FeO has been reduced to metallic iron, provided there is enough carbon [11] as is the case in the current system.

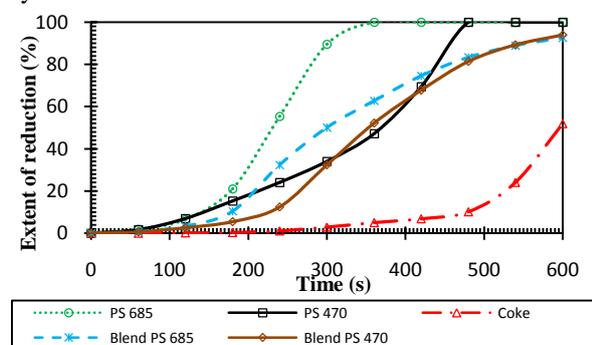


Fig. 8: Change in extent of reduction with time during the reduction of FeO in slag by various reductants at 1550 °C

An important distinguishing feature in the observed reduction behaviour of coke-PS blends worth mentioning here is that although blending resulted in significant improvement in reduction as was observed for coke-HDPE [3], coke-RT [4] and coke-PET [5] and coke-PP [6], the pure polymer in this case was superior to both coke and the blends as reductant, contrary to what was observed for the other polymers, but similar to the observations by Birol and Saridede who investigated the reduction behaviour of iron oxide by PET, coke and coke-PET blends at 1400 °C [14].

3.4 NATURE OF REDUCED METAL

Complete separation of the metal from slag is an important requirement for decreasing the levels of impurities in the reduced metal. Fig. 9 shows the nature of the metal produced from reduction of slag by Blend PS 685 at 1550 °C. Separation of the metal from slag improved with increasing levels of the polymer in the carbonaceous blend as was observed for coke-HDPE [3], coke-RT [4], coke-PET [5] and coke-PP blends [6].

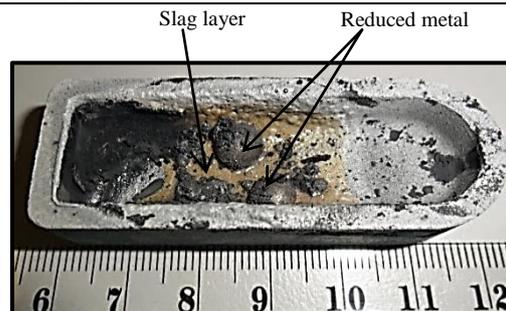


Fig. 9: Nature of metal produced from reduction of slag by (a) Blend PS 685 at 1550 °C

The XRD pattern of the reduced metal produced using PS 685 as a reductant is shown in Fig. 10, which shows distinct peaks of the metal along with the carbides.

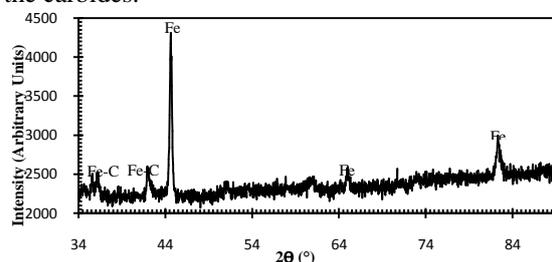


Fig. 10: XRD patterns of metal produced from reduction of slag by PS 685 at 1550 °C

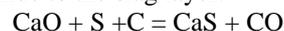
3.5 EFFECT OF PS BLENDING ON CARBURISATION AND DESULPHURISATION OF THE REDUCED METAL

Carburisation of the reduced metal is required for lowering its melting temperature and obtaining a melt-slag separation at molten state.

The contents of carbon and sulphur in the reduced metal were determined using a LECO Carbon/Sulphur analyser (model CS 230, LECO Corporation, Michigan, USA); the results are shown in Figs. 11 and 12 for carbon and sulphur respectively. Blending increased the content of carbon in the reduced metal from 0.650 wt. % (coke) to 4.38 wt. % and 4.88 wt. % for Blend PS 685 and Blend PS 470, respectively.

Blending also had a beneficial effect on sulphur removal from the reduced metal, declining significantly from 0.177 wt. % for coke to 0.01363 and 0.01862 for Blend PS 685 and Blend PS 470, respectively.

At this stage, the reason for the observed improvement in desulphurisation is not immediately apparent. As was explained in the work of Dankwah et al. [3-6] a decrease in the time required for the complete melting of the slag was again observed with an increase in the content of the polymer. Possibly, this improvement in the fluidity of the slag with polymer addition could promote the diffusion of calcium sulphide to the slag layer.



Using the sessile drop approach, Kongkarat [15] observed a reduction in sulphur pick up by iron when metallurgical coke was blended with bakelite, HDPE and PET.

IV. CONCLUSIONS

The reduction of FeO in EAF steelmaking slag by blends of coke and waste polystyrene (PS) has been investigated by experiments conducted in a laboratory-scale horizontal tube furnace; the major findings of the investigation are:

- (1) PS and blends of PS with coke could be used to partly or wholly replace the conventional coke used in iron and steelmaking as reductants and carburising agent.
- (2) Significant improvements in the extent of reduction were observed when coke was partly blended with PS.
- (3) The degree of carburisation of the reduced metal improved considerably when coke was blended with PS. It improved from 0.650 wt. % (coke) to 4.88 wt. % (Blend PS 470)
- (4) Blending resulted in a drastic decrease in sulphur from 0.177 wt. % (coke) to 0.01363 (Blend PS 685).

V. ACKNOWLEDGEMENTS

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