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Characterization and Optimization of Sorbents Utilized For Emission Control During Coal Gasification

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ABSTRACT

Advanced integrated gasification combined cycle and pressurized fluidized bed combustion power system requires both hot gas desulfurization and particulate filtration to improve system thermal efficiency and overall performance. Few metal oxides were evaluated to be the sorbent candidate for hot gas desulfurization process. Zinc oxide, zinc ferrite and zinc titanate had been tested in fixed bed and fluidized bed reactor. Zinc titanate sorbent was elected as the most promising sorbent candidate as it can efficiently reduce hydrogen sulfide to a low ppm level with an outstanding attrition resistance. Zinc oxide and zinc ferrite sorbents were disqualified mainly because the zinc vaporization and their physical degradation under temperature more than 500 degree C and mild reducing coal gas. However, the high capital investment for desulfurization and regeneration cycle as well as the high cost of zinc titanate sorbent and long term sorbent lost prevents it from commercial application.

The use of waste iron oxide as a disposable metal oxide sorbent will alleviate the constraints imposed on iron oxides including the degradation of sulfur capacity and its physical attrition required for a regenerable sorbent. The very low cost of waste iron oxides and the elimination of the investment associated with sorbent regeneration make it attractive to replace currently developed sorbent candidates. However, the use of waste iron oxides indicates a significant increase of dust loading for particulate filtration. The slower the reaction rate the iron oxide and coal ash mixture is, the longer residence time and higher iron oxide to coal ratio are required.

One of the key issue of the use of waste iron oxides as a disposable sorbent material relies on the capability of particulate filtration efficiency. The current back pulse cleaning of the dust cake had been evaluated; and the preliminary test results indicated that the simultaneous operation of hot gas desulfurization and particulate filtration is feasible.

A parametric testing will be performed on hot gas desulfurization and particulate independently first. The independent test results will help optimize the test design and evaluation of the integration of hot gas desulfurization testing and particulate filtration testing to be completed in the first two quarters 1998.

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1.0 Executive Summary

The development of hot gas desulfurization sorbents is one of the most critical issue for both IGCC and PFBC power systems. Zinc oxide, zinc ferrite and zinc titanate were the leading mixed metal oxides for hot gas desulfurization applications. These sorbents have high sulfur capacities and can remove hydrogen sulfide from coal gasifier gas down to less than 20 ppm. They can also be regenerated with inert-diluted air for multicycle operation.

Zinc oxide suffered from zinc vaporization and severe physical degradation problems under high temperature and mild reducing coal gas. Zinc ferrite sorbents prepared by granulation exhibited superior attrition resistance and long term chemical reactivity performance, but it is limited to a maximum temperature of about 550 degree C. Beyond that temperature, it tends to lose its mechanical strength due to excessive reduction and iron carbide formation.

Zinc titanate sorbents has shown higher durability than zinc ferrite and it can also withstand highly reducing fuel gas. In zinc titanate sorbent, zinc oxide is the only reactant agent, titanium oxide only help stabilize the sorbent performance. However, the high cost of zinc titanate sorbent and the capital investment of regeneration process makes the disposable iron oxides more attractive as hot gas desulfurization sorbent alternative.

The use of iron oxides material will increase the dust loading significantly. To maintain the normal operation of particulate filtration system, high dust cake permeability and the feasibility of dislodging a thicker layer of dust cake of iron oxide and coal ash mixture are mandatory.

In the subject study, hot gas desulfurization and particulate filtration were independently evaluated. Very heavy dust loading of coal as and iron oxide mixture dust cake were developed along the external surface of the candle filter; and the dust cake can be successfully dislodged with the use of back pulse cleaning technique. The preliminary success of the particulate filtration provides a assured foundation for the further study of the hot gas desulfurization and the integration testing of desulfurization and particulate removal.

The subject research will continue parametric studies on both hot gas desulfurization and particulate removal. The current dust loading exceeds the normal dust loading rate which will provides more room for a higher iron oxide to coal ash ratio for the dust mixture to compensate for the retarded chemical reaction or longer residence time if required.

Major parameters to be characterized for the joint testing of hot gas desulfurization and particulate filtration are deliberated in the report.

2.0 Introduction

Among the current hot gas cleanup technologies, PV A&M University is pursuing is the application of the dual use of waste iron oxide as a disposable sorbent and the aid additives in hot dusty gas stream requiring both desulfurization and enhanced particle removal efficiency at elevated temperatures. The innovative research work, to be performed at Prairie View A&M University, is to perform hot desulfurization and ambient filtration studies simultaneously which will prove the feasibility of an economical advancement of hot gas cleanup.

Current hot gas desulfurization research has demonstrated few regenerable sorbents are good candidates for desulfurization purpose. ZnO was found to be most suitable as it could reduce hydrogen sulfide in coal gas to a level of a few ppm depending on the temperature and steam content of coal gas. However under mild reducing environment, a significant decrease in crush strength and bulk density of ZnO pellets was reported. The deterioration of ZnO sorbent structure was derived from reduction of zinc oxide to zinc followed by vaporization of zinc. This limit set a threshold for the use of ZnO as sorbent for hot gas desulfurization at temperature above 500 degree C.

Iron oxide was investigated as a hot gas desulfurization sorbent since 1970s, and it has a high sulfur capacity and possesses high reactivity. In Japan iron oxide was developed as a hot gas desulfurization sorbent material using raw iron ore. However, iron oxide was report for degraded of the iron oxide sorbents due to excessive reduction and iron carbide formation under highly reducing conditions.

Zinc ferrite, an equimolar mixture of zinc oxide and iron oxide calcined at 800 to 850 degree C, was tested to remove hydrogen sulfide to a level less than 20 parts per million by volume (ppmv) over multiple desulfurization and regeneration cycles in a fixed bed reactor. Zinc ferrite also experienced excessive sorbent loss during desulfurization cycle even under moderately reducing coal gas.

Researchers then developed zinc titanate sorbent to resolve thermal stable and attrition difficulties experienced by other sorbent candidates. In zinc titanate sorbent, only zinc oxide is the reactive component of the sorbent, while titanium oxide provided stability to the sorbent by preventing zinc vaporization. But the high cost and problems of physical degradation and sintering at high temperature prevents it from commercial application for multiple desulfurization and regeneration cycles as planned

Recent economic evaluations have indicated that the thermal efficiency of IGCC systems can be optimized within an operation temperature range of 343 to 538 degree C. This temperature adjustment and the cost effective of the use of waste metal oxides make it feasible to develop an optimized hot gas desulfurization and hot particulate removal system for future applications. The key benefits rely on the use of the one time disposable of iron oxide, which will eliminate the attrition and degradation requirements for the reusable sorbents. The iron oxide additive will also help maintain high filtration permeability to compensate the increase of dust loading as continuous iron oxide feeding is required to serve as hydrogen sulfide removal sorbent. Therefore, it is crucial to ensure that the filtration capability and dust cake removal efficiency are sufficient to keep the hot gas cleanup system running smoothly and economically. An optimized particulate filtration system is mandatory to ensure the success of simultaneous of hot gas desulfurization and particulate filtration.

3.0 Results and Discussion

3.1 Characterization of ceramic filters

It is essential to characterize filter performance and filter permeability variations of unused and used filters to gain insights of particulate filtration and dust cake removal mechanism. Westinghouse and many research institutes had performed high temperature test on filters' thermal and physical properties. Since 1996, several filter manufacturers had made significant progress on the improvement of filter physical and thermal properties. Most of the filter materials available on the market are capable to stand thermal shock and long term thermal loading up to 800 degree C without losing much of its original strength. However, very few researches were conducted on filter permeability variations and dust cake removal mechanism. Therefore, at PV A&MU, permeability variations and changes of unused and used filters were evaluated within an innovative test setup assembled in the mechanical engineering laboratory at Prairie View A&MU. The schematic of a room ambient temperature filter test chamber is shown in **Figure 1**.

Ceramic filter samples were supplied by IF&P, Chicago, Illinois, 100.00 cm long, 3.81 cm I.D. and an O.D. of 6.35 cm. The other filter samples were provided by STC of Westinghouse. After the characterization of filter permeability variations, more study will be emphasized on the effect of maintaining high permeability of the dust cake of the mixture of iron oxide and coal ash. The mixture will be composed of different percentage of iron oxide vs coal ash. And the mixture will also be evaluated with size control parameter to optimize the range of the size of iron oxide to maximize dust cake permeability without increasing the frequency of back pulse cleaning even with significant increase of dust loading.

To facilitate room ambient testing on filter permeability variations, the test chamber vessel was made from a transparent plastic pipe. This test chamber vessel passed a 150.0 psig static pressure testing, compatible with Tidd APF pressure level. Ten 1/2 - 20 threaded holes are evenly spaced along the chamber axis to install fast response pressure transducers and the pressure calibrator to characterize the pressure field in the filter chamber during testing.

The candle filter is located along the center of the vessel axis to provide a cylindrical symmetrical system. A pressure sealing diaphragm and/or a solenoid valve was mechanically sealed on the top of the filter sealing assembly. The sealing diaphragm or the valve was later perforated or opened to characterize the chamber pressure per an ambient pressure test plan.

An advanced microprocessor based pressure calibrator was used with micro-machined silicon pressure transducers, installed along the axis of the filter test chamber, to characterize the variations of candle filter permeability and the gas stream pressure distribution field in the test chamber. A PC controlled data acquisition system was utilized to help collect test data.

After permeability data analysis, it appears that unused filters is characterized with a uniform permeability distribution along the entire filter surface areas; however, used filters displayed non-uniform permeability distribution pattern in both axial and circumferential directions as verified by other researchers. These filter permeability variations did create an uneven distributed velocity and pressure field. This uneven pressure field revealed the existence of an unexpected reversed gas flow field within a symmetric single filter test chamber.

The permeability variation test data demonstrated that the particulate removal efficiency attenuated in less porous areas than those of the other clean areas on the filter surface. The attenuated or blocked back pulse cleaning strength in the less porous filter surface areas caused undesirable dust cleaning barriers during the filtration cycle. These variations requires stronger back pulse to clean the dust patches away from the filter surface. This fact justifies that the need of an efficient back pulse system design to minimize the initial dust cake residues and the ensuing buildup of dust patches on top of the initial dust patches during the back pulse cleaning cycle.

3.2 Numerical thermal analysis

Thermal analysis was performed on a single filter during back pulse cleaning cycle with the use of commercial finite element code ANSYS (Version 5.0). The initial analysis was focused on the temperature distribution within filter during dust cake cleanup process. Half of a filter, cut along the vertical plane of symmetry, was used as the calculation domain. The module was developed by dividing the computation zone into five volumes. This multizone approach was used in order to overcome the difficulties in meshing due to high slenderness ratio (length to diameter) of the filter. Discretization of the computational zone was done using two types of 3-D elements from the ANSYS element library. The bottom closed end of the filter was meshed with 3-D 10-node tetrahedral thermal solid. The rest of the cylinder was meshed with 20-node Thermal Solid Brick. In total for the entire computation domain 3598 elements were used.

Connective boundary conditions were used for both outside and inside surface. The inside environmental temperature was assumed to be 40 degree C and the outside environment temperature was taken as 800 degree C, selected because it is close to the working temperature. 40 degree C at the inside was used to be close to the back pulse temperature. The convective heat transfer coefficients were obtained using correlation for forced flow. the thermal conductivity for the filter was taken as 87-86 W/mK, a value for silicon carbide.

The convective heat transfer coefficients used were 1105W/mK and 992 W/mK for inside and outside surface respectively. **Figure 2** shows the blow-up of the filter near the flange neck, the meshing of the elements and its temperature contour plot. The highest temperatures were on the outside surface close to the middle of the filter. The lowest temperature was on the inner surface close to the neck. The temperature variation ranges from 567 degree C to about 405 degree C.

3.3 Dust cake removal testing with back pulse

Hot Particulate Removal (HPR) is a critical issue for the subject simultaneous hot gas desulfurization and particulate filtration process. Filter reliability, solids loading and filter cleaning recovery, particle morphology, chemical reactions and temperature effect are the major research topics. Many research institutes and researchers have devoted their efforts in upgrading filter structures and its physical and chemical properties to survive chemical, steam and high temperature attack to improve filter reliability, durability and extend filter life time. Lately, researchers have realized the importance of the understanding of back pulse cleaning mechanism to resolve issues regarding filter permeability variations, ash bridging and micro-thermal cracks induced by thermal shock of cold back pulse cleaning, particle morphology and filter operating temperature.

In the past few months, dust cake of flour, mixture of flour and iron oxide, pure iron oxide and coal ash, originating from the Curtis-Wright PFBC facility, and its mixture with iron oxide have been successfully removed from IF&P ceramic filter with the use of back pulse cleaning. A parametric study on the ratio of iron oxide and coal ash of its mixture and the size effect of iron oxide on dust cake permeability and the ease of dust cake removal will be further studied at room ambient temperature prior to the integration testing of hot gas desulfurization and the particulate filtration.

Preliminary test results indicated that a specific threshold pulse pressure is required to clean the dust cake. Pulse pressure slightly above the threshold pressure seems strong enough to clean the dust cake over a short period of time. Excess dust loading may create residual dust layers along the filter surface, and the residual patch eventually needs higher pressure to dislodge the dust cake for the increased pressure drop through the dust cake. However, a initial stronger pulse pressure can provide a very clean filter surface after pulse cleaning; and the ensuing excess dust loading can be more effectively cleaned than the use of a initial weaker cleaning pulse pressure.

The key factor of the back pulse cleaning system appears to be the way to discharge a high momentum gas jet from a nozzle into the filter cavity. The momentum of the jet is transformed into a pressure increase inside the filter cavity. Based on the dust cake removal performance, it showed that high momentum jet can be achieved either with a large pipe diameter and a low pressure or with a small pipe diameter and high pulse pressure. The amount of the momentum converted into an increase of the pressure inside the filter cavity really depends on the design configuration of the back pulse cleaning setup. Because of the sharp increase of the dust loading of coal ash and iron oxide, a innovative back pulse cleaning setup with maximum mass flow rate will be explored for the rest of the subject research.

3.4 Evaluation of waste metal oxides for desulfurization sorbent candidates

Many researchers have learned that metal oxides can be used for hot gas desulfurization purpose. Due to the high cost of currently developed reusable sorbent candidates, people started to look into the use of waste metal oxides as an alternative for the removal of sulfur in hot gas cleaning. Typical sorbent candidate will cost more than $7.00/lb, which is two orders more expensive iron oxide ($0.07/lb), according to the analysis of IF&P. The new low operation temperature limit of 1,000 degree F makes the use of iron oxides as disposable sorbent candidates more attractive because the current research indicates this new approach is feasible. At PV A&MU, iron oxide powder will be evaluated with a parametric study on different operating temperature with different flowing velocity and powder size effect for hot gas desulfurization.

The subject research work will be continued on the factors of the following parameters in the first two quarters 1998 (according to the approval of the no cost extension): 1) the size effect of iron oxides on desulfurization and filtration performance, 2) iron oxides residing time for hot gas desulfurization with different face velocities (different residence time), 3) studies on the ratio of iron oxide loading to the ash loading, 4) studies on back pulse cleaning for ash and iron oxide mixture, and 5) studies on integration testing of hot desulfurization in a reducing atmosphere (use KRW gas) and ambient temperature filtration.

The proposed research work will be performed in seven phases:

- Phase I - Detail test plan generation (To be complete in January 1998)
- Phase II - Procurement and test setup modification of filter test chamber, finalize data acquisition and instrumentation system and the implementation of current hot gas desulfurization system to integrate it to the filter chamber for system testing (To be complete by early of February 1998)
- Phase III - Test Rig Setup (To be complete by middle February 1998)
- Phase IV - Independent testing on hot desulfurization and room ambient temperature filtration testing (oxide particle size, residence time and loading ratio of gas stream for dust cake removal) (To be complete by middle of March 1998)
- Phase V - Testing on hot desulfurization and filtration (To be complete by May 1998)
- Phase VI - Final Report (To be complete by June 1998)

4.0 Conclusion

The research work conducted in Q4 1997 was concentrated on the feasibility of using iron oxides in a simultaneous hot gas desulfurization and particulate filtration process. The preliminary test results indicated that the very heavy dust loading of iron oxide and coal ash mixture can be successfully dislodges with the use of back pulse cleaning technique. The past particulate filtration testing were repeated many times with a concentration more than 100,000 ppmw. The very high dust loading provides insights into the assurance of the feasibility of the use of iron oxides as a disposable sorbent candidate for hot gas desulfurization work.

An innovative design was completed to evaluate the reaction time and residence time required for iron oxide on hot gas desulfurization. Gas stream with controlled hydrogen sulfide concentration will be mixed with iron oxides matrix layer with preset reaction time to gain background of reaction time required to reduce hydrogen sulfide to a safe level. Different ratio of iron oxides to coal ash mixture will be used to evaluate the amount of iron oxides required in the coal ash and iron oxide mixtures to perform desulfirization task.

The use of disposable iron oxides as desulfurization sorbent candidate will mitigate many constraints imposed on current sorbent candidates. The less stringent operating temperature requirement will also justify the use of iron oxides as the low cost desulfurization sorbent candidate. The use of disposable sorbent can also eliminate the needs of sorbent regeneration process, saving a lot of initial capital investment and downstream operation and maintenance costs.

The significant capital, operation savings certainly justify various economical benefits of the simultaneous hot gas desulfurization and particulate filtration operation.

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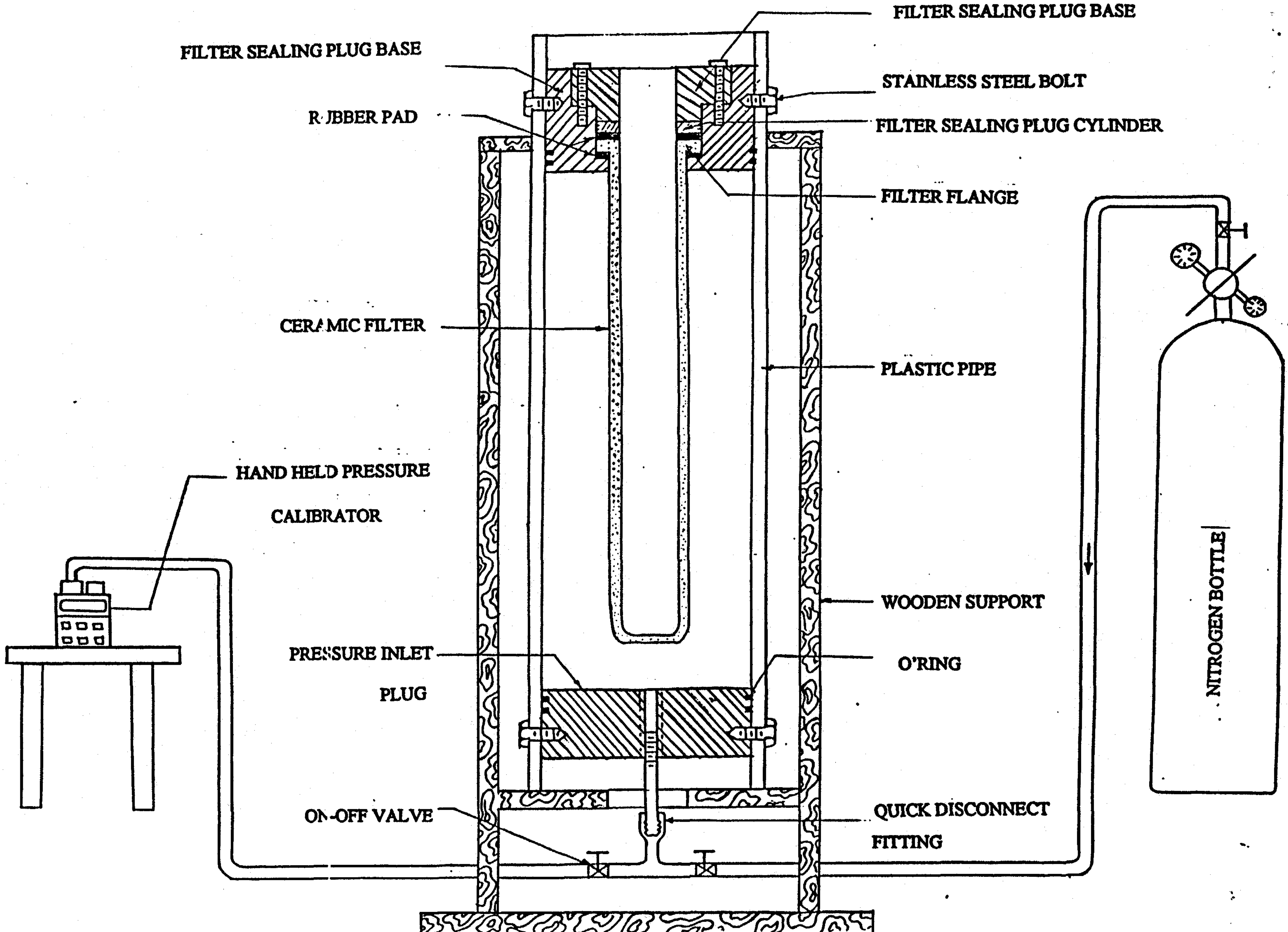

Fig 1 - SCHEMATIC DIAGRAM FOR USED AND UNUSED CERAMIC FILTER TEST

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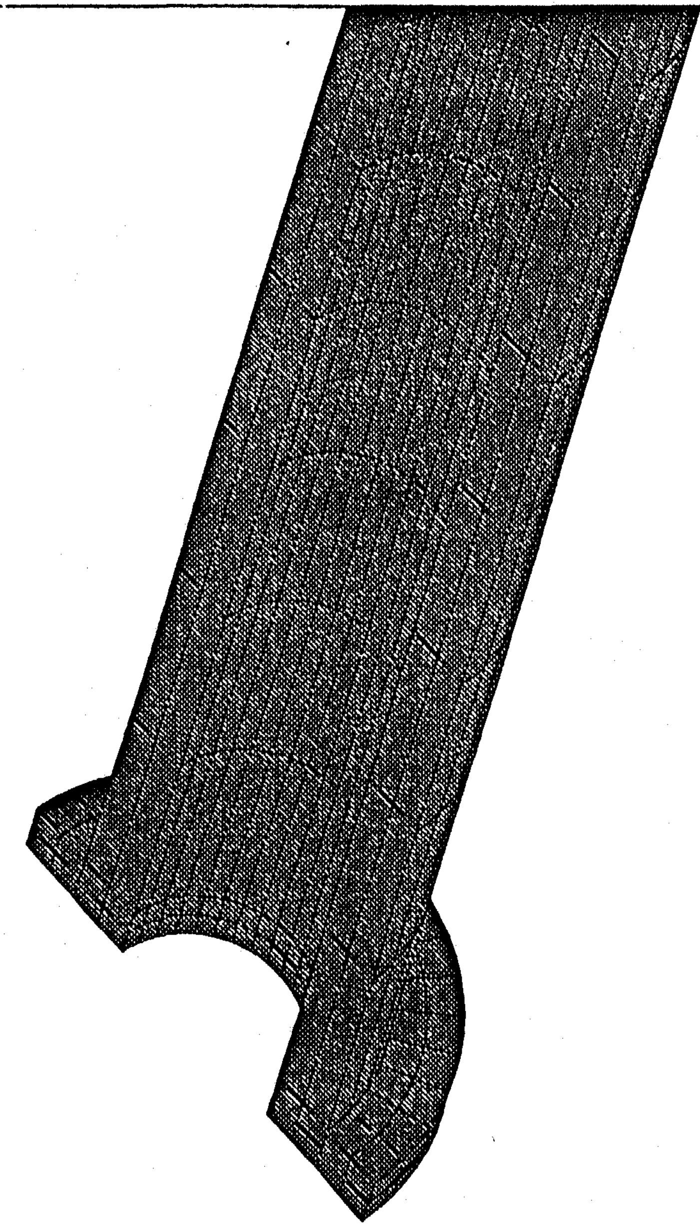

Fig 2 Blow up of the model (Filter) near the neck with element meshing